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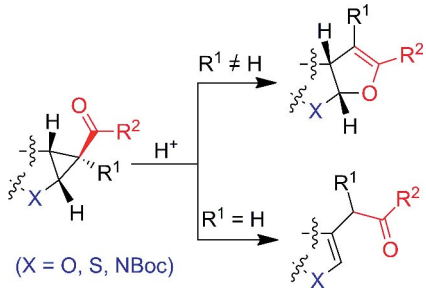
Strained Molecules

Brønsted acid catalyzed ring-enlargement and ring-opening reactions of donor-acceptor cyclopropanes with ketones as accepting unit and oxygen, sulfur and nitrogen as electron-donating moiety have been investigated. The mode of intramolecular rearrangement of the carbonyl-substituted cyclopropanes depends on subtle differences in the substitution pattern of the cyclopropane.



Keywords: Donor-acceptor systems / Strained molecules / Rearrangement / Heterocycles / Cyclopropanes

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Rearrangements of Furan-, Thiophene- and *N*-Boc-Pyrrole-Derived Donor-Acceptor Cyclopropanes: Scope and Limitations

Johannes Kaschel,[a] Tobias F. Schneider,[a] Patrick Schirmer,[a] Christian Maaß,[b] Dietmar Stalke,[b] and Daniel B. Werz*[c]

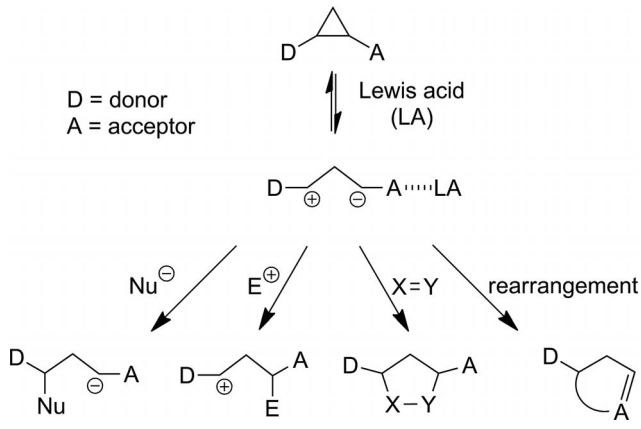
Keywords: Donor-acceptor systems / Strained molecules / Rearrangement / Heterocycles / Cyclopropanes

Rearrangements of furan-, thiophene- and *N*-Boc-pyrrole-derived donor–acceptor cyclopropanes initiated by Brønsted acids were investigated. Throughout the study, ketones or aldehydes were utilized as accepting moieties and oxygen, sulfur and Boc-protected nitrogen were used as the donor atoms. Whether a ring-enlargement and thus an annelation of a five-membered ring, or a ring-opening of the three-membered ring followed by rearomatization to the parent heterocycles takes place strongly depends on the substitution pattern of the cyclopropane. Commonly, more substituted substrates led to annelation whereas less substituted substrates tend to undergo rearomatization. In general, good yields were obtained for starting materials with oxygen and nitrogen donors, whereas the reactions with sulfur as donor gave only poor yields.

Introduction

The use of donor-acceptor (D-A) cyclopropanes as versatile building blocks in organic synthesis has become increasingly popular.[1–3] Activated by a Lewis acid (LA) and stabilized by specific substituents, 1,3-zwitterionic structures can be achieved through the heterolytic cleavage of the central C–C bond of the cyclopropane between the donating and the electron-withdrawing moieties.[1] This unique property not only enables reactions with nucleophiles (Nu), electrophiles (E), and olefins (X=Y), but also facilitates intramolecular rearrangement reactions in which the negatively polarized acceptor attacks the positively charged carbon atom adjacent to the donor. These possible reactions are summarized in Scheme 1.

For the synthesis of furan and dihydrofuran derivatives, intramolecular rearrangement reactions of D-A cyclopropanes have been used[4] and, recently, several examples were reported. A transformation developed by Müller and Chappellet employs diazopyruvates **1** and enol ethers **2** for a ruthenium-catalyzed synthesis of D-A cyclopropanes **3** that directly rearrange to give dihydrofurans **4**



Scheme 1. Common reactions of donor-acceptor (D-A) cyclopropanes.

(Scheme 2, a).[5] Another synthetic method was developed by Park et al. in 2012; these authors generated 2-aminofurans through the use of α-diazo-β-ketocarbonyls **5** and enamines **6** in a copper-mediated cyclopropanation reaction in the presence of oxygen. Again, rearrangement of the intermediate D-A cyclopropane **7** paves the way for the formation of product **9** (Scheme 2, b).[6]

Our previous investigations focused on aldehyde-substituted cyclopropanes annelated to a central furan core.[7] Subsequently, after preparation of the acceptors through oxidation of the respective alcohol functionalities, the desired ring-enlargement reactions took place to deliver the tricyclic bisacetal **12** (Scheme 3).[7] The corresponding ketones **13** do not undergo an instantaneous ring-enlargement and have been used by us as substrates for the preparation of 3,3′-linked bispyrroles[8] and bisthiophenes.[9]

[a] Institut für Organische und Biomolekulare Chemie, Georg-August-Universität Göttingen,
Tammannstr. 2, 37077 Göttingen, Germany
Fax: +49-55-399476
[b] Institut für Anorganische Chemie, Georg-August-Universität Göttingen,
Tammannstr. 4, 37077 Göttingen, Germany
[c] Institut für Organische Chemie, Technische Universität Braunschweig,
Hagenring 30, 38106 Braunschweig, Germany
E-mail: dwerz@tu-braunschweig.de
Homepage: http://werz.chemie.uni-goettingen.de
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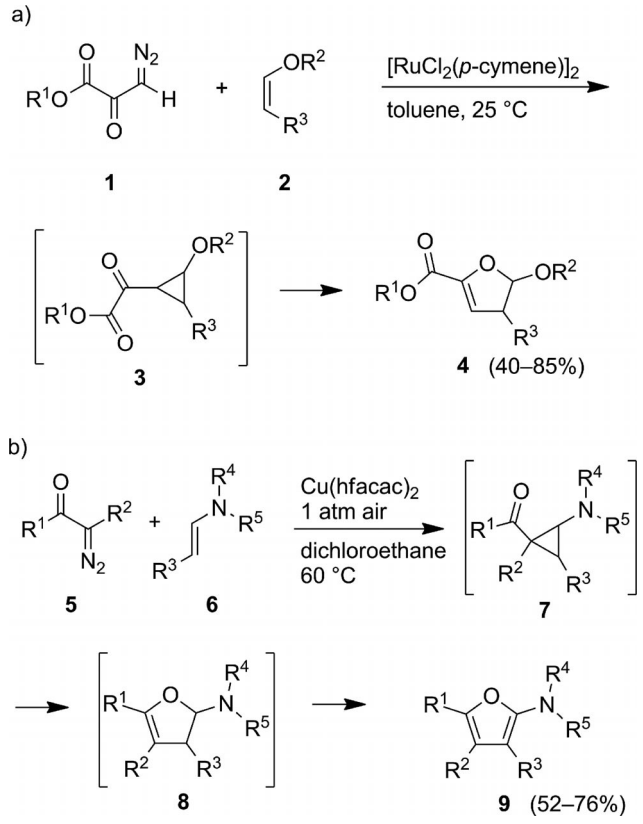


Scheme 2. Selected examples of the use of D-A cyclopropanes to access furan derivatives through intramolecular rearrangement.

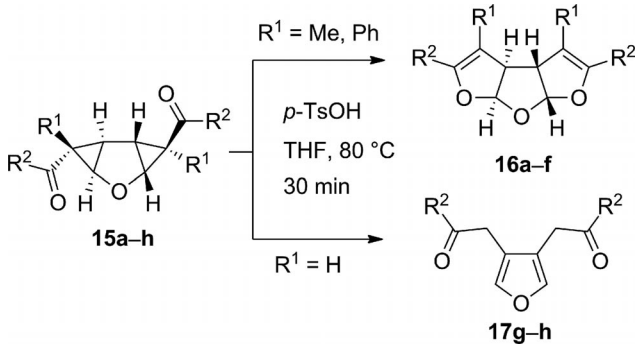
However, we assumed that the rearrangement of ketones can be triggered by the action of Lewis or Brønsted acids.

In this paper, we report on the possibility of using keto groups instead of aldehyde acceptors to enable an analogous reaction that leads to dihydrofuran units with one or two further substituents at the double bond. In addition, we also explore the possibility of employing donating units other than oxygen because previous theoretical studies have revealed that a variety of donor-acceptor combinations should lead to similar rearrangements.[10] Therefore, *N*-Boc-protected pyrrole and thiophene also served as starting materials for the reaction sequence starting with a cyclopropanation.

Results and Discussion

The attachment of a Lewis acid or a proton to the oxygen atom of a ketone moiety increases its electron-accepting capability. As mentioned above, compounds of type **15** are stable substrates, however, the three-membered rings rearrange upon the addition of catalytic amounts of *para*-toluenesulfonic acid (*p*TsOH) to a solution of **15** in hot tetrahydrofuran (THF). By this procedure tetrasubstituted tricyclic bisacetals of type **16** were obtained in very good yields (Table 1). Methyl and phenyl groups were employed as substituent R^1, directly attached to the three-membered ring; residue R^2 at the ketone moiety was varied from aliphatic and aromatic groups to heteroaromatic units. In all cases, good yields (71–94%) were obtained.

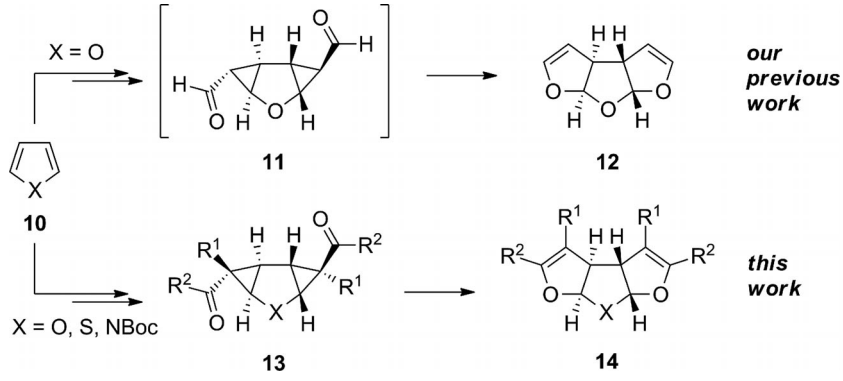
Table 1. Rearrangement reactions of diketones **15** to form tricyclic *O*,*O*-bisacetals of type **16** and furan derivatives of type **17** depending on the substitution pattern.



Entry	**15**	R^1	R^2	**16/17**	Yield [%] **16**	**17**
1	**a**	Me	Me	**a**	86	–
2	**b**	Me	2-furyl	**b**	94	–
3	**c**	Me	2-thienyl	**c**	75	–
4	**d**	Ph	Me	**d**	93	–
5[a]	**e**	Ph	2-furyl	**e**	71	–
6[a]	**f**	Ph	2-thienyl	**f**	87	–
7	**g**	H	*n*Pr	**g**	–	29
8[b]	**h**	H	Ph	**h**	–	60

[a] The reaction time was 2 h. [b] The reaction was performed in toluene.

However, when R^1 = H the outcome of the anticipated transformation was completely different; in this case, furan



Scheme 3. Rearrangements of carbonyl-substituted cyclopropanes built on furan, thiophene, or *N*-Boc-pyrrole.

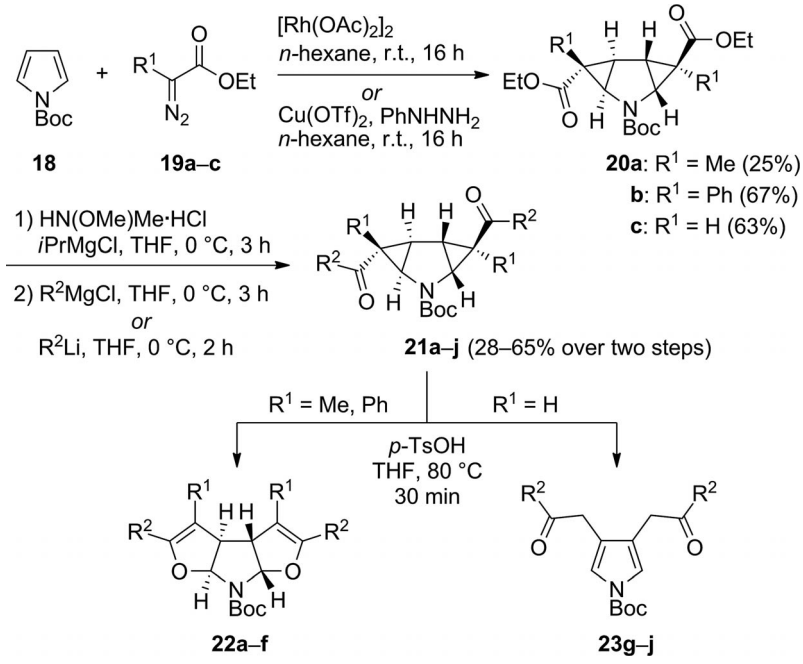
derivatives of type **17** were obtained (Table 1). Similar behavior was previously described by Wenkert and co-workers in the context of analogous ester-substituted cyclopropanes and is probably driven by the high energy gain released in the formation of the aromatic five-membered ring.[11]

To vary the heteroatom of the central ring, *N*-Boc-pyrrole (**18**) instead of furan was submitted to a twofold cyclopropanation reaction in the very first step.[12] As reaction partner, diazo compounds of type **19** were used; dirhodium tetraacetate or copper triflate were employed as catalyst. Despite the higher degree of aromaticity, twofold cyclopropanation took place smoothly and the tricyclic products were obtained in moderate to good yields (Table 2). In analogy to the preparation of the furan-derived substrates, the ester functionalities of **20** were converted into ketone units via the respective Weinreb amides. Depending on the substitution pattern, yields in the range of 28–65% were found for this two-step sequence. As mentioned previously, the rearrangement of the cyclopropanes was again initiated by the use of *para*-toluenesulfonic acid in hot THF, yielding products of type **22** (Table 2). Among the additional substituents R^1 attached to the cyclopropane rings of **21**, phenyl groups were slightly more beneficial for a successful rearrangement reaction than methyl groups. Furthermore, preparation of the methyl-substituted precursors (especially the cyclopropanation step) was much more demanding and gave lower yields. Similar to the formation of the furan derivative **17**, pyrrole derivatives of type **23** were obtained when R^1 = H.

The installation of different residues R^2 in the third step of the synthesis was achieved without significant problems. Neither aliphatic, aromatic nor heteroaromatic groups at this position led to remarkable changes in terms of the outcome of the rearrangement reaction.

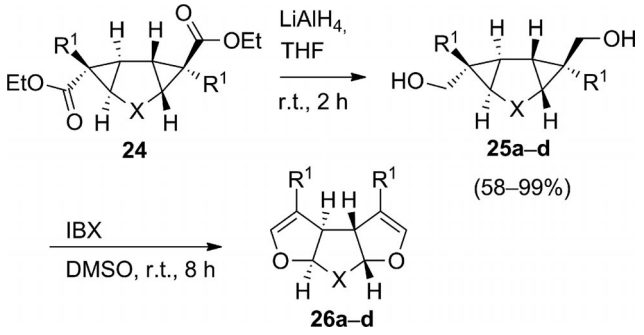
For cases in which the ester functionalities of **24** were converted into hydroxyl groups, an instantaneous ring-enlargement of **25** to tricycles of type **26** took place during the oxidation by 2-iodoxybenzoic acid (IBX) in dimethyl sulfoxide (DMSO). The residue R^2 of the previously described transformations is absent; thus, cyclic enol ethers with a substituent in only the 3-position were obtained in moderate yields (Table 3). The reaction proceeded well utilizing oxygen and Boc-protected nitrogen as donor atoms.

Table 2. Synthesis of tricyclic *N*,*O*-bisacetals **22** and pyrrole derivatives **23** starting from *N*-Boc-pyrrole (**18**).



Entry	**21**	R^1	R^2	**22/23**	Yield [%]	
					22	**23**
1	**a**	Me	Me	**a**	69	–
2	**b**	Me	2-thienyl	**b**	59	–
3	**c**	Ph	Me	**c**	97	–
4	**d**	Ph	*n*Pr	**d**	80	–
5	**e**	Ph	Ph	**e**	90	–
6	**f**	Ph	2-furyl	**f**	86	–
7	**g**	H	Me	**g**	–	90
8	**h**	H	*i*Pr	**h**	–	91
9	**i**	H	Ph	**i**	–	93
10	**j**	H	2-furyl	**j**	–	80

Table 3. Synthesis of **26** through oxidation of respective diols **25**.

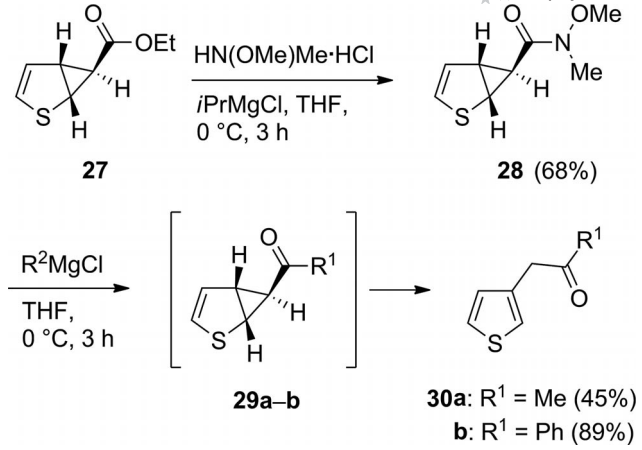


Entry	25	X	R^1	26	Yield [%]
1	**a**	O	Me	**a**	42
2	**b**	O	Ph	**b**	35
3	**c**	NBoc	H	**c**	42
4	**d**	NBoc	Ph	**d**	53

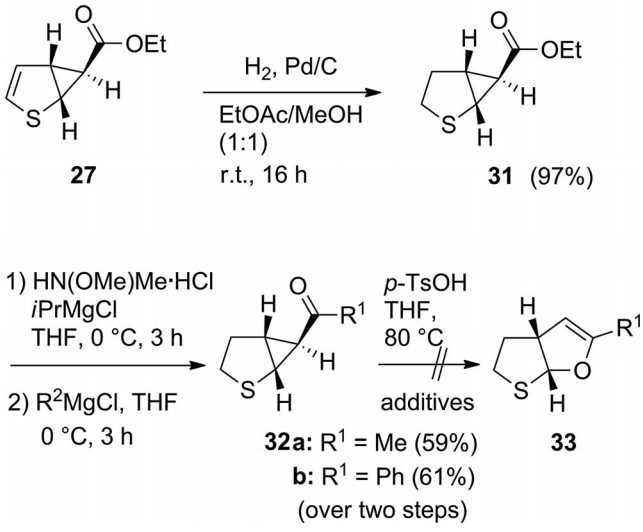
Our efforts to apply the presented strategies for the synthesis of *O*,*O*- and *N*,*O*-bisacetals to the corresponding thiophene derivatives proved to be a very challenging endeavor. To date, to the best of our knowledge, no practicable procedure with which to prepare doubly cyclopropanated thiophene has been reported, and we were also not able to solve this problem. All our attempts using different catalysts [e.g., copper(I) triflate, copper powder, dirhodium tetracetate, tetraphenylporphyrine ruthenium(II) carbonyl[13]] in varying solvents, at different temperatures and with a diverse range of diazo compounds were not successful. Even a second cyclopropanation of the previously reported monocyclopropanated thiophene **27**[14] did not work in our hands. Finally, we attempted to use **27** for the synthesis of bicyclic *S*,*O*-acetals, but the high tendency of thiophenes to rearomatization also prevented the success of this strategy. After formation of the Weinreb amide **28**, a Grignard reagent was added to install a keto group at the cyclopropane. This step initiated the instantaneous rearomatization of the thiophene by deconstruction of the three-membered ring, yielding only products of type **30** with aliphatic or aromatic substituents R^1 (Scheme 4).

We envisioned that a preceding hydrogenation of **27** could prevent rearomatization of the corresponding ketone **32**. Despite the presence of sulfur, the hydrogenation of the double bond by palladium on charcoal worked almost quantitatively. The synthesis of ketone **32** was accomplished by our common procedure (Scheme 5). The next step was to initiate the rearrangement of the cyclopropane to generate S,O-acetal **33**, however, the common procedure employing *para*-toluenesulfonic acid in hot THF failed. Addition of other Brønsted (H_2SO_4, HCl, F_3CCOOH) or Lewis acids [$MgCl_2$, $ZnCl_2$, $BF_3{\cdot}OEt_2$, $Yb(OTf)_3$] was ineffectual and did not transform **32** into **33**; in most cases the starting material was recovered.

The last possibility of inducing a rearrangement of the thiophene-derived cyclopropane was to install a stronger electron-withdrawing group at the three-membered ring.

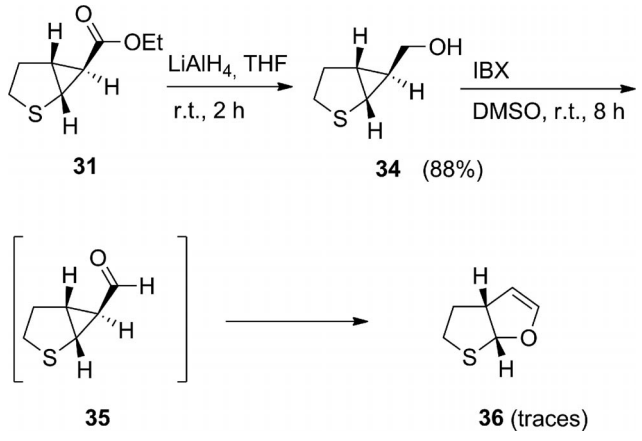


Scheme 4. Rearomatization of **29** to thiophene derivative **30**.



Scheme 5. Incomplete synthesis of bicyclic *S*,*O*-acetal **33**.

Therefore, hydrogenated compound **31** was subjected to our common two-step reduction/oxidation strategy. After treatment of alcohol **34** with 2-iodoxybenzoic acid (IBX)[15] in DMSO, the desired ring-enlargement took place; however, only trace amounts of monounsaturated bicyclic S,O-acetal **36** was formed (Scheme 6). Spectroscopic and mass spectro-



Scheme 6. Synthesis of the volatile *S*,*O*-acetal **36**.

metric data unequivocally confirmed the identity of this compound.

Single crystals of two D-A cyclopropanes **20b** and **21c** and one rearrangement product **26a** were obtained by crystallization from a mixture of *n*-hexane/dichloromethane at room temperature. X-ray diffraction experiments, conducted at 100 K,[16] were performed. Two molecular structures (**21c** and **26a**) are depicted in Figure 1. In both cases, the anti-orientation of the three annealed rings is confirmed. An elucidation of the geometrical properties within the three-membered rings of **20b** and **21c** shows an almost perpendicular arrangement of the electron-withdrawing ester (86.1° and 89.1° in **20b**) or the ketone unit (86.4° and 90.0° in **21c**), respectively, to the plane of the cyclopropane. Such a conformation is suggested by the Walsh model[17] of cyclopropane because optimal overlap between the π^*_{CO} and the HOMO of cyclopropane, being a combination of in-plane p orbitals, is reached. In addition, the bond lengths are in line with this model: the shortest bond [1.493(1) Å, 1.496(2) Å in **20b** and 1.491(2) Å, 1.492(2) Å in **21c**, respectively] is found opposite to the accepting unit. The longest bonds [1.542(2) Å, 1.542(1) Å in **20b** and 1.544(2) Å, 1.549(2) Å in **21c**] are located between the donor- and the acceptor-substituted carbon atoms.

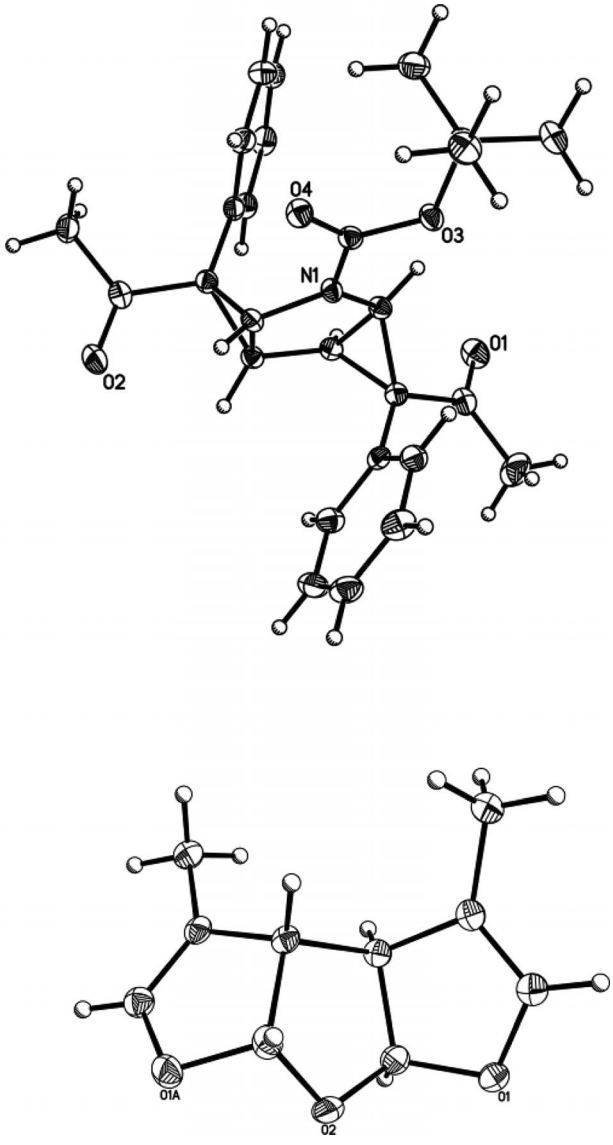


Figure 1. Molecular structures of **21c** (top) and **26a** (bottom) depicted with anisotropic displacement parameters at 50% probability level.

Conclusions

We have demonstrated that the simultaneous rearrangement of two donor-acceptor cyclopropanes is accomplished not only with furan-, but also with *N*-Boc-pyrrole-derived substrates. The short and simple procedure consisting of twofold cyclopropanation (even at the *N*-protected pyrrole), preparation of the Weinreb amides, and subsequent formation of the respective ketones followed by acid-mediated rearrangement delivers highly substituted tricyclic *O*,*O*- and *N*,*O*-bisacetals in very good yields. Less substituted congeners were accessible through our previously reported reduction/oxidation strategy. Substrates bearing a hydrogen atom at the cyclopropane adjacent to the acceptor group do not lead to annelated bisacetals but, instead, the parent five-membered aromatic heterocycle is regenerated by ring-opening of the cyclopropane.

Experimental Section

General Methods: All reactions were performed in flame-dried glassware under an argon atmosphere. The solvents were dried by standard procedures and distilled prior to use. Commercially available compounds were used without further purification unless otherwise stated. All products were obtained in purity higher than or equal to 95%. ^{1}H and ^{13}C NMR spectra were recorded with a 300, 500 or 600 MHz instrument using the residual signals from $CHCl_3$ (δ = 7.26 ppm and δ = 77.0 ppm), DMSO (δ = 2.54 ppm and δ = 40.45 ppm), and methanol (δ = 4.87 ppm and δ = 49.2 ppm), as internal reference. Assignments of the respective signals were made on the basis of a combination of H,H-COSY, HSQC and HMBC experiments. Unclear assignments are marked with a star '*'. HRMS (ESI) spectrometry was carried out with an FTICR instrument. IR spectra were measured with an ATR spectrometer. UV spectra were measured with a common photometer.

General Procedures

(A) Preparation of Bis-Weinreb Amides: To a solution of the diester (1.0 equiv.) in anhydrous THF (10 mL/mmol) was added *N*,*O*-dimethylhydroxylamine hydrochloride (3.5 equiv.) and then isopropylmagnesium chloride (2 M in THF, 5.0 equiv.) was slowly added at 0 °C. The mixture was stirred for 3 h at room temperature, quenched with satd. ammonium chloride solution, extracted with ethyl acetate (3 ×) and dried with sodium sulfate. The product was obtained after flash column chromatography on silica gel.

(B) Preparation of Diketones with Grignard Reagents: To a solution of the bis-Weinreb amide (1.0 equiv.) in anhydrous THF (10 mL/mmol) was added a solution of the Grignard reagent (2 or 3 M in THF or Et_2O, 3.0 equiv.) at 0 °C and the mixture was stirred for 3 h at room temperature. The mixture was quenched with satd. ammonium chloride solution, extracted with ethyl acetate (3 ×) and

dried with sodium sulfate. The product was obtained after flash column chromatography on silica gel.

(C) Preparation of Diketones with Lithiated Reagents: A solution of furan or thiophene (3.0 equiv.) in anhydrous THF (10 mL/mmol) was cooled to –78 °C and a solution of *tert*-butyllithium (1.6 M in pentane, 3.0 equiv.) was added. The mixture was stirred for 10 min at –78 °C, for 30 min at room temperature, and then cooled to 0 °C. After the addition of a solution of bis-Weinreb amide (1.0 equiv.) in anhydrous THF (10 mL/mmol), the mixture was stirred for 90 min at room temperature. The reaction was stopped by the addition of satd. ammonium chloride solution, extracted with ethyl acetate (3 ×) and dried with sodium sulfate. The product was obtained after flash column chromatography on silica gel.

(D) Preparation of Diols: To a suspension of lithium aluminum hydride (2.4 equiv.) in anhydrous THF (5 mL/mmol) at 0 °C was added a solution of the diester (1.0 equiv.) in anhydrous THF (5 mL/mmol), and the mixture was stirred for 2 h at room temperature. The reaction was stopped by the addition of methanol and purified by flash column chromatography on silica gel.

(E) Acid-Mediated Rearrangement of Diketones: A solution of diketone (1.0 equiv.) and *para*-toluenesulfonic acid monohydrate (5.0 mol-%) in THF (10 mL/mmol) was heated to 80 °C and stirred for 30 min at that temperature. The product was obtained after flash column chromatography on silica gel or basic aluminum oxide.

(F) Rearrangement Initiated by Oxidation: To a solution of diol (1.0 equiv.) in DMSO (10 mL/mmol) at room temperature was added 2-iodoxybenzoic acid (IBX; 2.4 equiv.) and the mixture was stirred for 8 h at room temperature. The reaction was stopped by the addition of water, filtered, extracted with ethyl acetate (3 ×), washed with water (3 ×), and dried with sodium sulfate. The product was obtained after flash column chromatography on silica gel.

Diketone 15e: Synthesized by using General Procedure C from bis-Weinreb amide **15e**-WA[8a] (100 mg, 236 μmol, 1.0 equiv.), furan (48 mg, 710 μmol, 3.0 equiv.), and *t*BuLi (1.6 M in pentane, 0.44 mL, 710 μmol, 3.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 3:1→2:1), yield 82 mg (188 μmol, 80%); yellow solid; R_f = 0.31 (hexane/EtOAc, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.69–2.92 (m, 2 H, 2,2′-H), 3.33–3.59 (m, 2 H, 1,1′-H), 5.37–5.52 (m, 2 H, 7,7′-H), 6.06–6.22 (m, 2 H, 6,6′-H), 7.34–7.43 (m, 2 H, 8,8′-H), 7.42–7.54 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 37.1 (C-2,2′), 43.7 (C-3,3′), 71.9 (C-1,1′), 111.6 (C-7,7′), 119.8 (C-6,6′), 128.5 (Ph_{tert}), 128.8 (Ph_{tert}), 132.3 (Ph_q), 132.9 (Ph_{tert}), 146.1 (C-8,8′), 151.2 (C-5,5′), 184.9 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1632, 1459, 1316, 1276, 1039 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 282 (4.57) nm. MS (ESI): *m*/*z* (%) = 437.2 (100) [M + H]$^+$, 459.1 (57) [M + Na]$^+$, 895.3 (55) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{28}H_{21}O_5$ [M + H]$^+$ 437.1384; found 437.1381.

Diketone 15f: Synthesized by using General Procedure C from bis-Weinreb amide **15f**-WA[8a] (111 mg, 263 μmol, 1.0 equiv.), thiophene (66 mg, 788 μmol, 3.0 equiv.), and *t*BuLi (1.6 M in pentane, 0.49 mL, 788 μmol, 3.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 5:1→4:1), yield 91 mg (194 μmol, 74%); yellow solid R_f = 0.59 (hexane/EtOAc, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.61–3.05 (m, 2 H, 2,2′-H), 3.28–3.59 (m, 2 H, 1,1′-H), 6.29–6.60 (m, 2 H, 7,7′-H), 6.63–6.95 (m, 2 H, 6,6′-H), 7.30–7.44 (m, 2 H, 8,8′-H), 7.46–7.73 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 37.8 (C-2,2′), 44.3 (C-3,3′), 72.5 (C-1,1′), 127.6 (C-7,7′), 128.6 (Ph_{tert}), 128.9 (Ph_{tert}), 132.4 (Ph_{quat}), 133.1 (Ph_{tert}), 133.5 (C-6,6′), 133.7 (C-8,8′), 143.8 (C-5,5′), 189.4 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1605, 1410, 1252, 1144, 1046 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 291 (4.04) nm. MS (ESI): *m*/*z* (%) = 469.1 (100) [M + H]$^+$, 491.1 (85) [M + Na]$^+$, 959.2 (51) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{28}H_{21}O_3S_2$ [M + H]$^+$ 469.0927; found 469.0926.

***O*,*O*-Bisacetal 16a:** Synthesized by using General Procedure E from diketone **15a**[8a] (22 mg, 106 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 5:1), yield 19 mg (91 μmol, 86%); white solid; R_f = 0.63 (hexane/EtOAc, 4:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56 (s, 6 H, Me), 1.71 (s, 6 H, Me), 3.17–3.34 (m, 2 H, 2,2′-H), 5.89 (d, *J* = 5.3 Hz, 2 H, 1,1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.8 (Me), 11.3 (Me), 54.7 (C-2,2′), 103.4 (C-3,3′), 106.6 (C-1,1′), 146.0 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 3445, 2920, 1703, 1386, 1188 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 199 (3.99) nm. MS (ESI): *m*/*z* (%) = 209.1 (40) [M + H]$^+$, 231.1 (75) [M + Na]$^+$, 439.3 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{12}H_{16}O_3Na$ [M + Na]$^+$ 231.0992; found: 231.0995.

***O*,*O*-Bisacetal 16b:** Synthesized by using General Procedure E from diketone **15b**[8b] (17 mg, 54 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 10 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 6:1→4:1), yield 16 mg (51 μmol, 94%); white solid; R_f = 0.59 (hexane/EtOAc, 6:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.04 (s, 6 H, Me), 3.60 (d, *J* = 5.6 Hz, 2 H, 2,2′-H), 6.13 (d, *J* = 5.6 Hz, 2 H, 1,1′-H), 6.40–6.46 (m, 2 H, 7,7′-H*), 6.52 (d, *J* = 3.3 Hz, 2 H, 6,6′-H*), 7.32–7.58 (m, 2 H, 8,8′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.2 (Me), 56.2 (C-2,2′), 106.0 (C-3,3′), 107.0, 108.9, 110.9 (C-1,1′,6,6′,7,7′), 139.7 (C-4,4′), 142.5 (C-8,8′), 146.5 (C-5,5′) ppm. IR (ATR): $\tilde{\nu}$ = 1487, 1326, 1159, 1096, 1078 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 275 (4.53). MS (ESI): *m*/*z* (%) = 313.1 (69) [M + H]$^+$, 335.1 (64) [M + Na]$^+$, 647.2 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{18}H_{16}O_5Na$ [M + Na]$^+$ 335.0890; found: 335.0893.

***O*,*O*-Bisacetal 16c:** Synthesized by using General Procedure E from diketone **15c**[8b] (36 mg, 104 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5.0 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 5:1), yield 27 mg (78 μmol, 75%); pale-yellow solid; R_f = 0.56 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (s, 6 H, Me), 3.64 (d, *J* = 5.1 Hz, 2 H, 2,2′-H), 6.14 (d, *J* = 5.1 Hz, 2 H, 1,1′-H), 7.06 (dd, *J* = 3.7, 5.0 Hz, 2 H, 7,7′-H), 7.19–7.58 (m, 4 H, 6,6′,8,8′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.1 (Me), 56.8 (C-2,2′), 105.2 (C-3,3′), 106.6 (C-1,1′), 125.6, 125.9, 127.0 (C-6,6′,7,7′,8,8′), 132.8 (C-5,5′), 143.0 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2965, 1664, 1433, 1319, 1093 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 294 (4.24) nm. MS (ESI): *m*/*z* (%) = 345.1 (80) [M + H]$^+$, 367.1 (22) [M + Na]$^+$. HRMS (ESI): calcd for $C_{18}H_{17}O_3S_2$ [M + H]$^+$ 345.0614; found: 345.0608.

***O*,*O*-Bisacetal 16d:** Synthesized by using General Procedure E from diketone **15d**[8a] (30 mg, 90 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 7:1), yield 28 mg (84 μmol, 93%); pale-yellow solid; R_f = 0.60 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.00 (s, 6 H, Me), 3.84–3.93 (m, 2 H, 2,2′-H), 6.10 (d, *J* = 5.9 Hz, 2 H, 1,1′-H), 6.87–7.54 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.1 (Me), 54.5 (C-2,2′), 106.7 (C-1,1′), 111.0 (C-3,3′), 126.3 (Ph_{tert}), 127.7 (Ph_{tert}), 128.4 (Ph_{tert}), 133.6 (Ph_{quat}), 149.2 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2972, 1664, 1496, 1385, 1337, 1202 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 262 (4.32) nm. MS (ESI): *m*/*z* (%) = 333.2 (66) [M + H]$^+$, 355.1 (70) [M + Na]$^+$, 687.3 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{22}H_{21}O_3$ [M + H]$^+$ 333.1485; found: 333.1485.

***O,O*-Bisacetal 16e:** Synthesized by using General Procedure E (reaction time 2 h) from diketone **15e** (31 mg, 71 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 5:1), yield 22 mg (50 μmol, 71%); yellow solid; R_f = 0.58 (hexane/EtOAc, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.05 (d, J = 5.3 Hz, 2 H, 2,2′-H), 6.25 (d, J = 5.3 Hz, 2 H, 1,1′-H), 6.38 (dd, J = 1.8, 3.4 Hz, 2 H, 7,7′-H), 6.60 (d, J = 3.4 Hz, 2 H, 6,6′-H), 6.95–7.65 (m, 12 H, 8,8′-H,Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.9 (C-2,2′), 106.6 (C-1,1′), 110.9, 111.1 (C-6,6′,7,7′), 111.4 (C-3,3′), 127.3 (Ph_{tert}), 128.2 (Ph_{tert}), 128.8 (Ph_{tert}), 132.4 (Ph_{quat}), 140.0 (C-4,4′), 142.9 (C-8,8′), 145.3 (C-5,5′) ppm. IR (ATR): $\tilde{\nu}$ = 2360, 1669, 1498, 1337, 1161 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 232 (4.39), 298 (4.32) nm. MS (ESI): *m*/*z* (%) = 437.2 (36) [M + H]$^+$, 459.2 (32) [M + Na]$^+$. HRMS (ESI): calcd for $C_{28}H_{21}O_5$ [M + H]$^+$ 437.1384; found: 437.1377.

***O,O*-Bisacetal 16f:** Synthesized by using General Procedure E (reaction time 2 h) from diketone **15f** (30 mg, 64 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 10 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 5:1→4:1), yield 26 mg (55 μmol, 87%); yellow solid; R_f = 0.66 (hexane/EtOAc, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.00 (d, J = 5.4 Hz, 2 H, 2,2′-H), 6.28 (d, J = 5.4 Hz, 2 H, 1,1′-H), 6.92 (dd, J = 3.8, 5.0 Hz, 2 H, 7,7′-H), 7.04–7.59 (m, 14 H, 6,6′,8,8′-H,Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 56.3 (C-2,2′), 106.6 (C-1,1′), 111.1 (C-3,3′), 126.5, 126.9, 127.2, 127.6 (C-6,6′,7,7′,8,8′,Ph_{tert}), 128.7 (Ph_{tert}), 128.9 (Ph_{tert}), 132.1, 132.8 (C-5,5′,Ph_{quat}), 143.6 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2972, 1646, 1327, 1243, 1191 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 235 (4.02), 305 (3.92) nm. MS (ESI): *m*/*z* (%) = 469.1 (81) [M + H]$^+$, 491.1 (74) [M + Na]$^+$. HRMS (ESI): calcd for $C_{28}H_{21}O_3S_2$ [M + H]$^+$ 469.0927; found: 469.0914.

1,1′-(Furan-3,4-diyl)bis(pentan-2-one) (17g): Synthesized by using General Procedure E from diketone **15g** (31 mg, 131 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5 mol-%). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 8:1→6:1), yield 9 mg (38 μmol, 29%); colorless oil; R_f = 0.40 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 7.4 Hz, 6 H, 7,7′-H), 1.41–1.74 (m, 4 H, 6,6′-H), 2.43 (t, J = 7.3 Hz, 4 H, 5,5′-H), 3.45 (s, 4 H, 3,3′-H), 7.34 (s, 2 H, 1,1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6 (C-7,7′), 17.2 (C-6,6′), 37.9 (C-3,3′), 43.9 (C-5,5′), 117.9 (C-2,2′), 141.3 (C-1,1′), 207.8 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2963, 1760, 1713, 1366, 1123 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 197 (3.68) nm. MS (ESI): *m*/*z* (%) = 237.2 (100) [M + H]$^+$, 259.1 (57) [M + Na]$^+$, 495.6 (35) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{14}H_{20}O_3Na$ [M + Na]$^+$ 259.1305; found: 259.1303.

2,2′-(Furan-3,4-diyl)bis(1-phenylethanone) (17h): Synthesized by using General Procedure E; the reaction was performed in toluene from diketone **15h** (30 mg, 99 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5 mol-%). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 3:1), yield 18 mg (59 μmol, 60%); white solid; R_f = 0.29 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.13 (s, 4 H, 3,3′-H), 6.90–8.16 (m, 12 H, 1,1′-H,Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.1 (C-3,3′), 118.4 (C-2,2′), 128.4 (Ph_{tert}), 128.6 (Ph_{tert}), 133.3 (Ph_{tert}), 136.4 (Ph_{quat}), 141.4 (C-1,1′), 197.1 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1767, 1685, 1596, 1448, 1213 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 194 (4.84), 241 (4.35) nm. MS (ESI): *m*/*z* (%) = 327.1 (58) [M + Na]$^+$, 631.2 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{20}H_{16}O_3Na$ [M + Na]$^+$ 327.0992; found: 327.0992.

Diester 20a: To a mixture of *N*-Boc-pyrrole (522 mg, 3.12 mmol, 1.0 equiv.) and $[Rh(OAc)_2]_2$ (28 mg, 62 μmol, 2 mol-%) in *n*-hexane (30 mL) was added a solution of 1-methyl ethyl diazoacetate[18] (**19a**; 2.00 g, 15.6 mmol, 5.0 equiv.) in *n*-hexane (8 mL) slowly by using a syringe pump (1 mL/h) at room temperature. The resulting mixture was stirred for further 8 h at room temperature and the product was obtained after flash column chromatography (SiO_2; pentane/EtOAc, 10:1→5:1), yield 288 mg (784 μmol, 25%); colorless oil; R_f = 0.47 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17–1.29 (m, 6 H, CH_2CH_3), 1.35 (s, 3 H, Me), 1.37 (s, 3 H, Me), 1.45 (s, 9 H, Me_{Boc}), 2.14–2.20 (m, 2 H, 2,2′-H), 3.32 (d, J = 6.5 Hz, 1 H, 1-H), 3.56 (d, J = 6.4 Hz, 1 H, 1′-H), 4.02–4.19 (m, 4 H, CH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 8.3, 8.4 (CH_2CH_3), 14.2 (Me), 14.2 (Me), 27.1, 27.4 (C-3,3′), 28.2 (Me_{Boc}), 28.5, 29.9 (C-2,2′), 47.8, 47.9 (C-1,1′), 60.9, 61.0 (CH_2CH_3), 80.8 ($C_{quat,Boc}$), 155.9 (CO_{Boc}), 172.4, 172.6 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1702, 1366, 1293, 1234, 1121 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 194 (4.17) nm. MS (ESI): *m*/*z* (%) = 390.2 (100) [M + Na]$^+$, 757.4 (41) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{19}H_{29}NO_6Na$ [M + Na]$^+$ 390.1887; found: 390.1890.

Diester 20b: To a solution of *N*-Boc-pyrrole (500 mg, 2.99 mmol, 1.0 equiv.) and $[Rh(OAc)_2]_2$ (13 mg, 30 μmol, 1.0 mol-%) in hexane (25 mL) was added a mixture of 1-phenyl ethyl diazoacetate[19] (1.71 g, 8.97 mmol, 3.0 equiv.) in hexane (3 mL) by using a syringe pump over a period of 80 min. The reaction was stirred at ambient temperature overnight, then the solvent was evaporated and the crude product was purified by flash column chromatography (SiO_2, pentane/EtOAc, 10:1→5:1), yield 981 mg (2.00 mmol, 67%); pale-yellow solid; R_f = 0.18 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03, 1.06 (t, J = 7.0 Hz, 6 H, Me), 1.51 (s, 9 H, Me_{Boc}), 2.58, 2.61 (d, J = 6.6 Hz, 2 H, 2,2′-H), 2.91, 3.03 (d, J = 6.6 Hz, 2 H, 1,1′-H), 3.90–4.04 (m, 4 H, CH_2), 7.21–7.41 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (Me), 28.4 (Me_{Boc}), 31.9, 33.0 (C-2,2′), 37.6, 37.7 (C-3,3′), 47.7, 47.8 (C-1,1′), 61.2, 61.2 (CH_2), 80.7 ($C_{q,Boc}$), 127.4, 127.5, 128.2, 128.4, 131.3, 131.6 (CH_{Ph}), 131.8, 131.9 (C_{Ph}), 154.4 (CO_{Boc}), 170.9, 171.1 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1708, 1696, 1414, 1246, 1235, 1124 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 258 (2.70) nm. MS (ESI): *m*/*z* (%) = 514.3 (94) [M + Na]$^+$, 1005.5 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{29}H_{33}NO_6Na$ [M + Na]$^+$ 514.2200; found: 514.2204.

Diester 20c: To a solution of *N*-Boc-pyrrole (5.00 g, 29.9 mmol, 1.0 equiv.), $Cu(OTf)_2$ (108 mg, 299 μmol, 1.0 mol-%), and $PhNHNH_2$ (29 μL, 32 mg, 299 μmol, 1.0 mol-%) in hexane (50 mL) was added a mixture of ethyl diazoacetate (11.0 g, 96.3 mmol, 3.2 equiv.) in CH_2Cl_2 (500 mL) by using a dropping funnel over a period of 8 h and stirred at room temp. overnight. Purification: Column chromatography (SiO_2; pentane/EtOAc, 8:1→5:1), yield 6.38 g (18.8 mmol, 63%); slightly yellow oil; R_f = 0.16 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16–1.25 (m, 6 H, Me), 1.42 (s, 9 H, Me_{Boc}), 1.72 (m_c, 2 H, 3,3′-H), 2.31 (br. s, 2 H, 2,2′-H), 3.40 (m_c, 2 H, 1,1′-H), 3.99–4.14 (m, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (Me), 27.7, 29.0 (C-2,2′), 27.8 (C-3,3′), 28.3 (Me_{Boc}), 42.2 (1,1′), 60.8 (CH_2), 80.9 ($C_{q,Boc}$), 154.2 (CO_{Boc}), 170.0, 170.3 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1702, 1413, 1286, 1165, 1150, 1120, 1019 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 195 (4.01), 209 (4.02) nm. MS (ESI): *m*/*z* (%) = 362.2 (62) [M + Na]$^+$, 701.4 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{17}H_{25}NO_6Na$ [M + Na]$^+$ 362.1574; found 362.1568.

Bis-Weinreb Amide 20a-WA: Synthesized by using General Procedure A (reaction time 12 h) from diester **20a** (250 mg, 680 μmol, 1.0 equiv.), *N,O*-dimethylhydroxylamine hydrochloride (332 mg, 3.40 mmol, 5.0 equiv.), and isopropylmagnesium chloride (2 M in THF, 2.72 mL, 5.44 mmol, 8.0 equiv.). Purification: flash column chromatography (SiO_2; EtOAc), yield 168 mg (423 μmol, 62%);

pale-yellow oil. R_f = 0.28 (EtOAc). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 6 H, Me), 1.47 (s, 9 H, Me_{Boc}), 2.14 (d, J = 6.8 Hz, 1 H, 2-H), 2.23 (d, J = 6.7 Hz, 1 H, 2′-H), 3.12–3.47 (m, 8 H, 1,1′-H,NMe), 3.73 (s, 3 H, OMe), 3.75 (s, 3 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 10.0 (Me), 10.1 (Me), 24.7, 26.3 (C-2,2′), 28.3 (Me_{Boc}), 28.9, 29.1 (C-3,3′), 34.0, 34.1 (NMe), 44.8, 44.8 (C-1,1′), 60.8, 60.9 (OMe), 80.5 ($C_{quat,Boc}$), 156.0 (CO_{Boc}), 171.2, 171.8 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2976, 1697, 1644, 1411, 1169, 1124 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 200 (4.28) nm. MS (ESI): m/z (%) = 420.2 (100) [M + Na]$^+$, 817.5 (69) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{19}H_{31}N_3O_6Na$ [M + Na]$^+$ 420.2105; found 420.2108.

Bis-Weinreb Amide 20b-WA: Synthesized by using General Procedure A from diester **20b** (366 mg, 745 μmol, 1.0 equiv.), *N*,*O*-dimethylhydroxylamine hydrochloride (363 mg, 3.72 mmol, 5.0 equiv.), and isopropylmagnesium chloride (2 M in THF, 2.05 mL, 4.10 mmol, 5.5 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 277 mg (531 μmol, 71%); white solid foam; R_f = 0.21 (hexane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (s, 9 H, Me_{Boc}), 2.39, 2.55 (d, J = 6.8 Hz, 2 H, 2,2′-H), 2.95, 2.97 (d, J = 6.4 Hz, 2 H, 1,1′-H), 3.03, 3.07 (s, 6 H, NMe), 3.16, 3.32 (s, 6 H, OMe), 7.21–7.42 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.6 (Me_{Boc}), 29.4, 30.8 (C-2,2′), 33.7, 33.8 (NMe), 38.7, 39.1 (C-3,3′), 45.9, 46.2 (C-1,1′), 60.2, 60.4 (OMe), 80.4 ($C_{q,Boc}$), 127.2, 127.2, 128.1, 128.2, 131.1, 131.3 (CH_{Ph}), 133.1, 133.4 (C_{Ph}), 154.9 (CO_{Boc}), 169.5, 170.0 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1695, 1638, 1418, 1365, 1176, 1126 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 194 (5.01) nm. MS (ESI): m/z (%) = 544.3 (100) [M + Na]$^+$, 1065.6 (51) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{29}H_{35}N_3O_6Na$ [M + Na]$^+$ 544.2418; found 544.2419.

Bis-Weinreb Amide 20c-WA: Synthesized by using General Procedure A from diester **20c** (5.00 g, 14.7 mmol, 1.0 equiv.), *N*,*O*-dimethylhydroxylamine hydrochloride (7.19 g, 73.7 mmol, 5.0 equiv.), and isopropylmagnesium chloride (2 M in THF, 40.5 mL, 81.0 mmol, 5.5 equiv.). Purification: Column chromatography (SiO_2; pentane/EtOAc, 3:1→1:2), yield 3.58 g (9.69 mmol, 66%); white solid; R_f = 0.21 (CH_2Cl_2/MeOH, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, Me_{Boc}), 2.30 (br s, 2 H, 2,2′-H), 2.39–2.46 (m, 2 H, 3,3′-H), 3.14–3.21 (m, 6 H, NMe), 3.41 (m_c, 2 H, 1,1′-H), 3.76 (s, 6 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.6 (C-3,3′), 27.3, 28.6 (C-2,2′), 28.4 (Me_{Boc}), 32.3 (NMe), 42.8 (C-1,1′), 61.6 (OMe), 80.6 ($C_{q,Boc}$), 154.4 (CO_{Boc}), 169.9, 170.2 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1693, 1636, 1416, 1393, 1123 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 208 (4.36) nm. MS (ESI): m/z (%) = 370.2 (9) [M + H]$^+$, 392.2 (16) [M + Na]$^+$, 761.4 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{17}H_{27}N_3O_6Na$ [M + Na]$^+$ 392.1792; found 392.1788.

Diketone 21a: Synthesized by using General Procedure B from bis-Weinreb amide **20a**-WA (89 mg, 224 μmol, 1.0 equiv.) and methylmagnesium chloride (3 M in THF, 373 μL, 1.12 mmol, 5.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 1:1), yield 53 mg (172 μmol, 77%); pale-yellow solid; R_f = 0.47 (hexane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42–1.48 (15 H, Me_{Boc},Me), 2.21–2.35 (m, 8 H, 2,2′-H,Me), 3.21 (d, J = 6.4 Hz, 1 H,1-H), 3.41 (d, J = 6.4 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.6 (Me), 28.3 (Me_{Boc}), 28.3 (Me), 30.3, 31.6 (C-2,2′), 34.5, 34.8 (C-3,3′), 50.5, 50.6 (C-1,1′), 80.9 ($C_{quat,Boc}$), 155.6 (CO_{Boc}), 206.7, 206.9 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1706, 1675, 1390, 1361, 1228, 1125 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 229 (4.03) nm. MS (ESI): m/z (%) = 330.2 (100) [M + Na]$^+$, 637.3 (51) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{17}H_{25}NO_4Na$ [M + Na]$^+$ 330.1676; found 330.1674.

Diketone 21b: Synthesized by using General Procedure C from bis-Weinreb amide **20a**-WA (75 mg, 189 μmol, 1.0 equiv.), thiophene (48 mg, 566 μmol, 3.0 equiv.), and *t*BuLi (1.6 M in pentane, 0.35 mL, 566 μmol, 3.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 4:1), yield 60 mg (135 μmol, 71%); yellow solid; R_f = 0.31 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.52 (s, 9 H, Me_{Boc}), 1.59 (s, 3 H, Me), 1.62 (s, 3 H, Me), 2.41–2.50 (m, 2 H, 2,2′-H), 3.41–3.57 (m, 2 H, 1,1′-H), 7.08–7.18 (m, 2 H, 7,7′-H), 7.57–7.66 (m, 2 H, 6,6′-H*), 7.83–8.06 (m, 2 H, 8,8′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.7 (Me), 11.7 (Me), 26.0, 27.2 (C-2,2′), 28.3 (Me_{Boc}), 34.5, 34.5 (C-3,3′), 47.0, 47.1 (C-1,1′), 81.0 ($C_{quat,Boc}$), 127.6, 128.1 (C-7,7′), 132.9, 133.2, 133.4, 133.5 (C-6,6′,8,8′), 142.4, 142.4 (C-5,5′), 155.8 (CO_{Boc}), 191.7, 191.7 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2974, 1697, 1603, 1391, 1252, 1122 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 261 (4.22), 289 (4.22) nm. MS (ESI): m/z (%) = 466.1 (78) [M + Na]$^+$. HRMS (ESI): calcd for $C_{23}H_{25}NO_4S_2Na$ [M + Na]$^+$ 466.1117; found 466.1119.

Diketone 21c: Synthesized by using General Procedure B from bis-Weinreb amide **20b**-WA (248 mg, 476 μmol, 1.0 equiv.) and methylmagnesium chloride (3 M in THF, 0.63 mL, 1.90 mmol, 4.0 equiv.). Purification: Column chromatography (SiO_2; pentane/EtOAc, 8:1→5:1), yield 189 mg (438 μmol, 92%); white solid; R_f = 0.34 (hexane/EtOAc, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 9 H, Me_{Boc}), 1.86, 1.87 (s, 6 H, Me), 2.60, 2.66 (d, J = 6.4 Hz, 2 H, 2,2′-H), 2.81, 2.87 (d, J = 6.4 Hz, 2 H, 1,1′-H), 7.21–7.47 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.5 (Me_{Boc}), 30.0, 30.0 (Me), 33.7, 34.9 (C-2,2′), 45.7, 45.8 (C-3,3′), 50.5, 50.5 (C-1,1′), 80.9 ($C_{q,Boc}$), 127.9, 128.0, 128.9, 129.1, 131.4, 131.7 (CH_{Ph}), 133.3, 133.5 (C_{Ph}), 154.3 (CO_{Boc}), 204.9, 205.3 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1699, 1680, 1408, 1217, 1126 cm^{-1}. UV (CH_3CN): λ_{max} no absorbance maximum between 190 and 350 nm. MS (ESI): m/z (%) = 454.2 (66) [M + Na]$^+$, 885.5 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{27}H_{29}NO_4Na$ [M + Na]$^+$ 454.1989; found 454.1995.

Diketone 21d: Synthesized by using General Procedure B from bis-Weinreb amide **20b**-WA (139 mg, 266 μmol, 1.0 equiv.) and *n*-propylmagnesium chloride (2 M in Et_2O, 0.47 mL, 931 μmol, 3.5 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 6:1→5:1), yield 58 mg (119 μmol, 45%); white solid; R_f = 0.46 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.51–0.80 (m, 6 H, 7,7′-H), 1.20–1.41 (m, 4 H, 6,6′-H), 1.49 (s, 9 H, Me_{Boc}), 1.89–2.30 (m, 4 H, 5,5′-H), 2.50–2.70 (m, 2 H, 2,2′-H), 2.70–2.92 (m, 2 H, 1,1′-H), 6.99–7.60 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.4, 13.5 (C-7,7′), 16.9, 17.1 (C-6,6′), 28.4 (Me), 33.4, 34.5 (C-2,2′), 43.5, 43.7 (C-5,5′), 45.5, 45.6 (C-3,3′), 50.3, 50.5 (C-1,1′), 80.8 ($C_{quat,Boc}$), 127.9, 127.9, 128.9, 129.0, 131.6, 132.0 (Ph_{tert}), 133.1, 133.2 (Ph_{quat}), 154.4 (CO_{Boc}), 206.8, 207.3 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2967, 1702, 1683, 1409, 1162, 1122 cm^{-1}. UV (CH_3CN): λ_{max} no absorbance maximum between 190 and 350 nm. MS (ESI): m/z (%) = 488.3 (25) [M + H]$^+$, 510.3 (60) [M + Na]$^+$, 997.5 (60) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{31}H_{37}NO_4Na$ [M + Na]$^+$ 510.2615; found 510.2610.

Diketone 21e: Synthesized by using General Procedure B from bis-Weinreb amide **20b**-WA (55 mg, 105 μmol, 1.0 equiv.) and phenylmagnesium chloride (2 M in THF, 0.18 mL, 368 μmol, 3.5 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 6:1), yield 42 mg (76 μmol, 72%); white solid; R_f = 0.28 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.62 (s, 9 H, Me_{Boc}), 2.77–2.85 (m, 2 H, 2,2′-H), 3.13 (d, J = 6.6 Hz, 1 H, 1-H), 3.25 (d, J = 6.5 Hz, 1 H, 1′-H), 6.99–7.85 (m, 20 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.6 (Me_{Boc}), 31.7, 32.0 (C-2,2′), 44.9, 45.5 (C-3,3′), 49.1, 49.6 (C-1,1′), 81.2 ($C_{quat,Boc}$), 127.7, 127.8, 127.8,

127.8, 128.6, 128.7, 128.7, 128.9, 131.5, 131.5, 131.8, 132.1 (Ph_{tert}), 133.0, 133.1, 137.4, 137.8 (Ph_{quat}), 154.9 (CO_{Boc}), 197.9, 198.4 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1697, 1668, 1415, 1243, 1120 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 244 (4.32) nm. MS (ESI): *m/z* (%) = 456.2 (10) $[M + H]^+$, 578.2 (50) $[M + Na]^+$, 1133.5 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{37}H_{33}NO_4Na$ $[M + Na]^+$ 578.2302; found 578.2303.

Diketone 21f: Synthesized by using General Procedure C from bis-Weinreb amide **20b**-WA (109 mg, 209 µmol, 1.0 equiv.), furan (43 mg, 627 µmol, 3.0 equiv.), and *t*BuLi (1.6 M in pentane, 0.39 mL, 627 µmol, 3.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 2:1), yield 73 mg (136 µmol, 65%); pale-yellow solid; R_f = 0.33 (hexane/EtOAc, 2:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 9 H, Me_{Boc}), 2.79 (d, *J* = 6.4 Hz, 1 H, 2-H), 2.85 (d, *J* = 6.4 Hz, 1 H, 2′-H), 2.95–3.23 (m, 2 H, 1,1′-H), 5.48 (dd, *J* = 0.6, 3.7 Hz, 1 H, 7-H), 5.63 (dd, *J* = 0.7, 3.7 Hz, 1 H, 7′-H), 6.12–6.18 (m, 2 H, 6,6′-H), 7.30–7.64 (m, 12 H, 8,8′-H,Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 (Me_{Boc}), 34.4, 36.1 (C-2,2′), 43.9, 44.0 (C-3,3′), 51.2, 51.4 (C-1,1′), 81.1 ($C_{quat,Boc}$), 111.6, 111.7 (C-6,6′*), 120.0, 120.0 (C-7,7′*), 128.5, 128.6, 128.9, 129.1 (Ph_{tert}), 132.4 (Ph_{quat}), 132.5 (Ph_{tert}), 132.5 (Ph_{quat}), 132.7 (Ph_{tert}), 146.3, 146.3 (C-8,8′), 151.1, 151.2 (C-5,5′), 154.5 (CO_{Boc}), 184.6, 184.9 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2360, 1702, 1631, 1388, 1264, 1120 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 283 (4.01) nm. MS (ESI): *m/z* (%) = 536.2 (34) $[M + H]^+$, 558.2 (100) $[M + Na]^+$, 1093.4 (97) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{33}H_{29}NO_6Na$ $[M + Na]^+$ 558.1887; found 558.1884.

Diketone 21g: Synthesized by using General Procedure B from bis-Weinreb amide **20c**-WA (200 mg, 716 µmol, 1.0 equiv.) and methylmagnesium chloride (3 M in THF, 0.72 mL, 2.15 mmol, 3.0 equiv.). Purification: Column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 179 mg (64.2 µmol, 90%); white solid; R_f = 0.25 (hexane/EtOAc, 2:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, Me_{Boc}), 2.08 (br s, 2 H, 2,2′-H), 2.27 (s, 6 H, Me), 2.41 (br s, 2 H, 3,3′-H), 3.36 (m_c, 2 H, 1,1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 (Me_{Boc}), 29.7, 31.0 (C-2,2′), 31.0 (Me), 30.6, 30.7 (C-3,3′), 45.0, 45.1 (C-1,1′), 81.0 ($C_{q,Boc}$), 154.0 (CO_{Boc}), 203.7, 203.8 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1697, 1681, 1390, 1166, 1121 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 228 (4.05) nm. MS (ESI): *m/z* (%) = 302.2 (100) $[M + Na]^+$, 581.3 (71) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{15}H_{21}NO_4Na$ $[M + Na]^+$ 302.1363; found 302.1363.

Diketone 21h: Synthesized by using General Procedure B from bis-Weinreb amide **20c**-WA (103 mg, 279 µmol, 1.0 equiv.) and isopropylmagnesium chloride (2 M in THF, 0.70 mL, 1.39 mmol, 5.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 39 mg (116 µmol, 42%); white solid; R_f = 0.30 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.97–127 (m, 12 H, 6,6′,6a,6a′-H), 1.44 (s, 9 H, Me_{Boc}), 2.06–2.19 (m, 2 H, 2,2′-H), 2.31–2.54 (m, 1 H, 3,3′-H), 2.63–2.90 (m, 2 H, 5,5′-H), 3.14–3.51 (m, 2 H, 1,1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 17.5, 17.9, 18.0, 18.5 (C-6,6′,6a,6a′), 28.3 (Me_{Boc}), 29.1, 30.4 (C-3,3′), 33.9, 34.2 (C-2,2′), 41.7, 41.8 (C-5,5′), 44.9, 45.3 (C-1,1′), 80.9 ($C_{quat,Boc}$), 154.1 (CO_{Boc}), 209.7, 210.0 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2967, 1697, 1677, 1390, 1120, 1041 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 229 (4.06) nm. MS (ESI): *m/z* (%) = 336.2 (7) $[M + H]^+$, 358.2 (93) $[M + Na]^+$, 693.4 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{19}H_{29}NO_4Na$ $[M + Na]^+$ 358.1989; found 358.1987.

Diketone 21i: Synthesized by using General Procedure B from bis-Weinreb amide **20c**-WA (106 mg, 287 µmol, 1.0 equiv.) and phenylmagnesium chloride (2 M in THF, 0.72 mL, 1.43 mmol, 5.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 6:1→4:1), yield 97 mg (240 µmol, 84%); white solid; R_f = 0.30 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 9 H, Me_{Boc}), 2.59–3.11 (m, 4 H, 2,2′,3,3′-H), 3.43–4.00 (m, 2 H, 1,1′-H), 7.34–8.17 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.3 (Me_{Boc}), 30.6, 31.4, 32.6, 33.1 (C-2,2′,3,3′), 46.2 (C-1,1′), 81.2 ($C_{quat,Boc}$), 128.0, 128.6 (Ph_{tert}), 133.2 (Ph_{quat}), 137.2 (Ph_{tert}), 154.3 (CO_{Boc}), 196.0 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1694, 1651, 1391, 1289, 1121, 1022 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 199 (4.78), 245 (4.46) nm. MS (ESI): *m/z* (%) = 404.2 (9) $[M + H]^+$, 426.2 (47) $[M + Na]^+$, 829.4 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{25}H_{25}NO_4Na$ $[M + Na]^+$ 426.1676; found 426.1673.

Diketone 21j: Synthesized by using General Procedure C from bis-Weinreb amide **20c**-WA (79 mg, 214 µmol, 1.0 equiv.), furan (44 mg, 642 µmol, 3.0 equiv.), and *t*BuLi (1.6 M in pentane, 0.40 mL, 642 µmol, 3.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 2:1→1:1), yield 46 mg (120 µmol, 56%); yellow solid; R_f = 0.31 (hexane/EtOAc, 2:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 9 H, Me_{Boc}), 2.57–2.84 (m, 4 H, 2,2′,3,3′-H), 3.42–3.78 (m, 2 H, 1,1′-H), 6.42–6.66 (m, 2 H, 7,7′-H), 7.15–7.23 (m, 2 H, 6,6′-H), 7.53–7.65 (m, 2 H, 8,8′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.3 (Me), 30.1, 31.3, 32.4, 32.6 (C-2,2′,3,3′), 45.5 (C-1,1′), 81.2 ($C_{quat,Boc}$), 112.5, 116.9 (C-6,6′,7,7′), 146.5, 146.7 (C-8,8′), 152.7 (C-5,5′), 154.2 (CO_{Boc}), 184.5 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1691, 1642, 1406, 1168, 1118 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 279 (4.57) nm. MS (ESI): *m/z* (%) = 384.1 (10) $[M + H]^+$, 406.1 (60) $[M + Na]^+$, 789.3 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{21}H_{21}NO_6Na$ $[M + Na]^+$ 406.1261; found 406.1267.

***N*,*O*-Bisacetal 22a:** Synthesized by using General Procedure E from diketone **21a** (43 mg, 140 µmol, 1.0 equiv.) and *p*TsOH·H_2O (1.5 mg, 7 µmol, 5.0 mol-%). Purification: Filtration through basic Al_2O_3, flash column chromatography (SiO_2; pentane/EtOAc, 10:1), yield 30 mg (97 µmol, 69%); yellow oil; R_f = 0.30 (hexane/EtOAc, 10:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.83–1.40 (m, 21 H, Me,-Me,Me_{Boc}), 3.19 (d, *J* = 6.3 Hz, 2 H, 2,2′-H), 5.74–6.11 (m, 2 H, 1,1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.7 (2 Me), 11.3 (Me), 11.4 (Me), 28.3 (Me_{Boc}), 53.6, 54.2 (C-2,2′), 80.7 ($C_{quat,Boc}$), 90.6, 90.7 (C-1,1′), 103.4 (C-3,3′), 146.0, 146.4 (C-4,4′), 153.8 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 2975, 1709, 1365, 1168, 1138 cm^{-1}. UV (CH_3CN): λ_{max} no absorbance maximum between 190 and 350 nm. MS (ESI): *m/z* (%) = 308.2 (8) $[M + H]^+$, 330.2 (73) $[M + Na]^+$, 637.3 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{17}H_{25}NO_4Na$ $[M + Na]^+$ 330.1676; found 330.1681.

***N*,*O*-Bisacetal 22b:** Synthesized by using General Procedure E from diketone **21b** (34 mg, 77 µmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 µmol, 5 mol-%). Purification: Filtration through basic Al_2O_3, flash column chromatography (SiO_2; pentane/EtOAc, 8:1), yield 19 mg (43 µmol, 59%); white solid; R_f = 0.39 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.55 (s, 9 H, Me_{Boc}), 1.97 (s, 6 H, Me), 3.52–3.65 (m, 2 H, 2,2′-H), 5.98–6.28 (m, 2 H, 1,1′-H), 6.97–7.36 (m, 6 H, 6,6′,7,7′,8,8′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 11.0 (Me), 28.3 (Me_{Boc}), 55.2, 56.1 (C-2,2′), 80.9 ($C_{quat,Boc}$), 90.5 (C-1,1′), 105.2 (C-3,3′*), 125.4 (C-7,7′*), 126.0 (C-6,6′), 126.9 (C-8,8′*), 133.0, 133.3 (C-5,5′), 142.6, 143.1 (C-4,4′), 153.2 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 3086, 1703, 1381, 1146, 1089 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 209 (4.18), 297 (4.34) nm. MS (ESI): *m/z* (%) = 466.1 (48) $[M + Na]^+$, 909.2 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{23}H_{25}NO_4S_2Na$ $[M + Na]^+$ 466.1117; found 466.1120.

***N*,*O*-Bisacetal 22c:** Synthesized by using General Procedure E from diketone **21c** (31 mg, 72 µmol, 1.0 equiv.) and *p*TsOH (1 mg,

5 μmol, 5 mol-%). Purification: Column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 30 mg (70 μmol, 97%); white solid; R_f = 0.45 (hexane/EtOAc, 2:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.57 (s, 9 H, Me_{Boc}), 1.88, 1.91 (br s, 6 H, Me), 3.85 (m_c, 2 H, 2,2′-H), 6.08 (m_c, 2 H, 1,1′-H), 7.00–7.07 (m, 4 H, Ph), 7.18–7.26 (m, 2 H, Ph), 7.27–7.36 (m, 4 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.9, 13.1 (Me), 28.4 (Me_{Boc}), 52.7, 53.4 (C-2,2′), 81.1 ($C_{q,Boc}$), 90.4, 90.5 (C-1,1′), 110.8, 110.9 (C-3,3′), 126.0, 126.0, 127.8, 127.9, 128.2, 128.2 (CH_{Ph}), 133.7, 133.7 (C_{Ph}), 149.0, 149.5 (C-4,4′), 153.6 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 1717, 1677, 1379, 1167 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 264 (4.22) nm. MS (ESI): *m/z* (%) = 454.2 (93) $[M + Na]^+$, 885.5 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{27}H_{29}NO_4Na$ $[M + Na]^+$ 454.1989; found 454.1987.

***N,O*-Bisacetal 22d:** Synthesized by using General Procedure E from diketone **21d** (35 mg, 72 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5 mol-%). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 10:1→8:1), yield 28 mg (57 μmol, 80%); colorless oil; R_f = 0.61 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82–1.00 (m, 6 H, 7,7′-H), 1.46–1.68 (m, 13 H, 6,6′-H,Me_{Boc}), 2.13–2.36 (m, 4 H, 5,5′-H), 3.86 (d, *J* = 6.9 Hz, 2 H, 2,2′-H), 5.90–6.19 (m, 2 H, 1,1′-H), 6.99–7.41 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.5, 13.7 (C-7,7′), 20.2, 20.4 (C-6,6′), 28.2 (C-5,5′), 28.3 (Me_{Boc}), 52.4, 53.1 (C-2,2′), 80.7 ($C_{quat,Boc}$), 89.9, 90.1 (C-1,1′), 110.9 (C-3,3′), 126.1, 127.1, 128.3 (Ph_{tert}), 133.9 (Ph_{quat}), 152.5, 153.1 (C-4,4′), 153.5 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 2962, 1716, 1379, 1242, 1165 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 265 (4.17) nm. MS (ESI): *m/z* (%) = 488.3 (3) $[M + H]^+$, 510.3 (34) $[M + Na]^+$, 997.6 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{13}H_{37}NO_4Na$ $[M + Na]^+$ 510.2615; found 510.2608.

***N,O*-Bisacetal 22e:** Synthesized by using General Procedure E from diketone **21e** (29 mg, 52 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 10 mol-%). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 8:1), yield 26 mg (47 μmol, 90%); white solid; R_f = 0.53 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.68 (s, 9 H, Me_{Boc}), 4.05 (d, *J* = 7.2 Hz, 2 H, 2,2′-H), 6.10–6.38 (m, 2 H, 1,1′-H), 6.93–7.49 (m, 20 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 (Me_{Boc}), 53.7, 54.5 (C-2,2′), 81.1 ($C_{quat,Boc}$), 89.9 (C-1,1′), 111.6 (C-3,3′), 126.9, 127.7, 127.9, 128.6, 128.7, 128.8 (Ph_{tert}), 130.6, 133.6 (Ph_{quat}), 148.1, 148.5 (C-4,4′), 153.5 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 1715, 1377, 1134, 1065, 1019 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 224 (4.50), 293 (4.33) nm. MS (ESI): *m/z* (%) = 578.2 (35) $[M + Na]^+$, 1133.5 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{37}H_{33}NO_4Na$ $[M + Na]^+$ 578.2302; found 578.2303.

***N,O*-Bisacetal 22f:** Synthesized by using General Procedure E from diketone **21f** (29 mg, 54 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 10 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 5:1), yield 25 mg (47 μmol, 86%); white solid; R_f = 0.44 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (s, 9 H, Me_{Boc}), 4.01 (d, *J* = 6.7 Hz, 2 H, 2,2′-H), 6.02–6.59 (m, 6 H, 1,1′,6,6′,7,7′-H), 7.07–7.36 (m, 12 H, 8,8′-H,Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.4 (Me_{Boc}), 53.7, 54.5 (C-2,2′), 81.3 ($C_{quat,Boc}$), 90.3 (C-1,1′), 110.4, 110.9, 111.5 (C-3,3′,6,6′,7,7′), 127.1, 128.2, 129.0 (Ph_{tert}), 132.5 (Ph_{quat}), 142.8 (C-4,4′), 142.8 (C-8,8′), 145.7 (C-5,5′), 153.3 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 2360, 1713, 1377, 1157, 1082 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 233 (4.45), 298 (4.40) nm. MS (ESI): *m/z* (%) = 536.4 (8) $[M + H]^+$, 558.4 (62) $[M + Na]^+$, 1093.7 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{33}H_{29}NO_6Na$ $[M + Na]^+$ 558.1887; found 558.1889.

Pyrrole 23g: Synthesized by using General Procedure E from diketone **21g** (50.0 mg, 179 μmol, 1.0 equiv.) and *p*TsOH (1.5 mg, 9.0 μmol, 5 mol-%). Stirred overnight (12 h) at room temperature. Purification: Column chromatography (SiO_2; pentane/EtOAc, 4:1→3:1), yield 45 mg (161 μmol, 90%); slightly yellow oil; R_f = 0.37 (hexane/EtOAc, 2:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.56 (s, 9 H, Me_{Boc}), 2.16 (s, 6 H, Me), 3.45 (s, 4 H, CH_2), 7.11 (s, 2 H, 1,1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.0 (Me_{Boc}), 29.2 (Me), 40.8 (CH_2), 83.7 ($C_{q,Boc}$), 119.1 (C-2,2′), 119.2 (C-1,1′), 148.3 (CO_{Boc}), 206.0 (CO) ppm. IR (ATR): $\tilde{\nu}$ = 1710, 1366, 1252, 1150 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 236 (3.94) nm. MS (ESI): *m/z* (%) = 302.1 (75) $[M + Na]^+$, 581.3 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{13}H_{21}NO_4Na$ $[M + Na]^+$ 302.1363; found 302.1363.

Pyrrole 23h: Synthesized by using General Procedure E from diketone **21h** (30 mg, 89 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5.0 mol-%). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 27 mg (81 μmol, 90%); colorless oil; R_f = 0.37 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.82–1.21 (m, 12 H, 6,6′,6a,6a′-H), 1.56 (s, 9 H, Me_{Boc}), 2.52–2.91 (m, 2 H, 5,5′-H), 3.51 (s, 4 H, 3,3′-H), 7.08 (s, 2 H, 1,1′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.4 (C-6,6′,6a,6a′), 28.0 (Me_{Boc}), 37.7 (C-3,3′), 40.0 (C-5,5′), 83.5 ($C_{quat,Boc}$), 119.2 (C-1,1′), 119.6 (C-2,2′), 148.5 (CO_{Boc}), 212.0 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2972, 1710, 1367, 1252, 1153 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 230 (3.91) nm. MS (ESI): *m/z* (%) = 336.2 (27) $[M + H]^+$, 358.2 (73) $[M + Na]^+$, 693.4 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{19}H_{29}NO_4Na$ $[M + Na]^+$ 358.1989; found 358.1983.

Pyrrole 23i: Synthesized by using General Procedure E from diketone **21i** (28 mg, 69 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 5 mol-%). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 6:1), yield 26 mg (64 μmol, 93%); white solid; R_f = 0.35 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.54 (s, 9 H, Me_{Boc}), 4.12 (s, 4 H, 3,3′-H), 7.15 (s, 2 H, 1,1′-H), 7.34–8.32 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.9 (Me_{Boc}), 35.8 (C-3,3′), 83.4 ($C_{quat,Boc}$), 119.3 (C-1,1′), 119.8 (C-2,2′), 128.3, 128.5, 133.1 (Ph_{tert}), 136.4 (Ph_{quat}), 148.4 (CO_{Boc}), 197.5 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2977, 1731, 1682, 1369, 1210, 1151 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 197 (4.77), 241 (4.54), 317 (2.44) nm. MS (ESI): *m/z* (%) = 404.2 (34) $[M + H]^+$, 426.2 (28) $[M + Na]^+$, 829.4 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{25}H_{25}NO_4Na$ $[M + Na]^+$ 426.1676; found 426.1670.

Pyrrole 23j: Synthesized by using General Procedure E from diketone **21j** (20 mg, 52 μmol, 1.0 equiv.) and *p*TsOH·H_2O (1 mg, 5 μmol, 10 mol-%). Purification: flash column chromatography (basic Al_2O_3; pentane/EtOAc, 2:1→1:1), yield 16 mg (42 μmol, 80%); yellow oil; R_f = 0.43 (hexane/EtOAc, 2:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.53 (s, 9 H, Me_{Boc}), 3.96 (s, 4 H, 3,3′-H), 6.47–6.57 (m, 2 H, 7,7′-H), 7.14 (s, 2 H, 1,1′-H), 7.21–7.29 (m, 2 H, 6,6′-H), 7.55–7.58 (m, 2 H, 8,8′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.9 (Me_{Boc}), 35.4 (C-3,3′), 83.5 ($C_{quat,Boc}$), 112.3 (C-7,7′), 117.8 (C-6,6′), 119.1 (C-2,2′), 119.4 (C-1,1′), 146.5 (C-8,8′), 148.4 (CO_{Boc}), 152.2 (C-5,5′), 186.4 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 1733, 1670, 1466, 1368, 1253, 1151 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 267 (4.48) nm. MS (ESI): *m/z* (%) = 384.1 (26) $[M + H]^+$, 406.1 (28) $[M + Na]^+$, 789.3 (100) $[2M + Na]^+$. HRMS (ESI): calcd for $C_{21}H_{21}NO_6$ $[M + Na]^+$ 406.1261; found 406.1267.

Diol 25a: Synthesized by using General Procedure D from diester **24a**[8a] (170 mg, 634 μmol, 1.0 equiv.) and $LiAlH_4$ (58 mg, 1.52 mmol, 2.4 equiv.). Purification: flash column chromatography (SiO_2; CH_2Cl_2/MeOH, 8:1), yield 111 mg (603 μmol, 95%); white solid; R_f = 0.21 (CH_2Cl_2/MeOH, 10:1). ^1H NMR (300 MHz, CD_3OD): δ = 1.29 (s, 6 H, Me), 1.42 (d, *J* = 5.9 Hz, 2 H, 2,2′-H), 3.06–3.20 (m, 4 H, 4,4′-H), 3.39 (d, *J* = 5.9 Hz, 2 H, 1,1′-H), 4.84

(br s, 2 H, OH) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ = 10.3 (Me), 26.2 (C-2,2′), 27.9 (C-3,3′), 67.8 (C-4,4′), 68.0 (C-1,1′) ppm. IR (ATR): $\tilde{\nu}$ = 3340, 1496, 1325, 1154, 1008 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 194 (4.81) nm. MS (ESI): *m/z* (%) = 331.1 (100) [M + Na]$^+$, 639.3 (90) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{20}H_{20}O_3Na$ [M + Na]$^+$ 331.1305; found 331.1305.

Diol 25c: Synthesized by using General Procedure D from diester **20c** (500 mg, 1.47 mmol, 1.0 equiv.) and $LiAlH_4$ (123 mg, 3.24 mmol, 2.2 equiv.). Purification: Column chromatography (SiO_2; CH_2Cl_2/MeOH, 30:1→10:1), yield 372 mg (1.46 mmol, 99%); colorless foam; R_f = 0.21 (CH_2Cl_2/MeOH, 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20–1.30 (m, 2 H, 2,2′-H), 1.43 (s, 9 H, Me_{Boc}), 1.57–1.72 (m, 2 H, 3,3′-H), 2.75–2.92 (m, 2 H, 1,1′-H), 3.14–3.53 (m, 6 H, CH_2, OH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 23.9, 25.5 (C-3,3′), 28.5 (Me_{Boc}), 29.4, 29.5 (C-2,2′), 39.2, 39.8 (C-1,1′), 62.1 (CH_2), 80.2 ($C_{q,Boc}$), 155.7 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 3355, 1661, 1437, 1391, 1364, 1122, 1025 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 195 (3.98) nm. MS (ESI): *m/z* (%) = 256.2 (3) [M + H]$^+$, 278.2 (33) [M + Na]$^+$, 511.4 (21) [2M + H]$^+$, 533.3 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{13}H_{21}NO_4Na$ [M + Na]$^+$ 278.1363; found 278.1366.

Diol 25d: Synthesized by using General Procedure D from diester **20b** (506 mg, 1.03 mmol, 1.0 equiv.) and $LiAlH_4$ (78 mg, 2.06 mmol, 2.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 1:1), yield 244 mg (599 µmol, 58%); white solid; R_f = 0.13 (hexane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.49 (s, 9 H, Me_{Boc}), 1.84, 1.87 (d, *J* = 6.6 Hz, 2 H, 2,2′-H), 2.45 (d, *J* = 6.6 Hz, 1 H, 1-H), 2.51 (d, *J* = 6.6 Hz, 1 H, 1′-H), 2.53 (br s, 2 H, OH), 3.15–3.39 (m, 4 H, CH_2), 7.23–7.39 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.3, 28.5 (C-2,2′), 28.5 (Me_{Boc}), 37.5, 37.8 (C-3,3′), 44.4, 44.4 (C-1,1′), 68.4, 68.5 (CH_2), 80.0 ($C_{q,Boc}$), 126.8, 127.1, 128.3, 128.6, 130.7, 131.0 (CH_{Ph}), 135.7, 135.9 (C_{Ph}), 155.4 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 3368, 1649, 1440, 1124 cm^{-1}. UV (CH_3CN): λ_{max} no maximum of absorption in the effective range (190–350 nm). MS (ESI): *m/z* (%) = 430.2 (63) [M + Na]$^+$, 815.5 (24) [2M + H]$^+$, 837.5 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{25}H_{29}NO_4Na$ [M + Na]$^+$430.1989; found 430.1986.

***O,O*-Bisacetal 26a:** Synthesized by using General Procedure F from diol **25a** (97 mg, 527 µmol, 1.0 equiv.) and IBX (354 mg, 1.26 mmol, 2.4 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 40 mg (222 µmol, 42%); white solid; R_f = 0.63 (hexane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.63 (s, 6 H, Me), 3.21–3.37 (m, 2 H, 2,2′-H), 5.94–6.07 (m, 4 H, 1,1′,4,4′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.5 (Me), 53.1 (C-2,2′), 108.6 (C-1,1′), 110.6 (C-3,3′), 138.5 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2969, 1711, 1669, 1304, 1114 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 202 (3.98) nm. MS (ESI): *m/z* (%) = 203.1 (77) [M + Na]$^+$, 383.1 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{10}H_{12}O_3Na$ [M + Na]$^+$ 203.0679; found 203.0679.

***O,O*-Bisacetal 26b:** Synthesized by using General Procedure F from diol **25b** (245 mg, 794 µmol, 1.0 equiv.) and IBX (489 mg, 1.75 mmol, 2.2 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 6:1), yield 83 mg (273 µmol, 34%); white solid; R_f = 0.48 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.98 (d, *J* = 5.4 Hz, 2 H, 2,2′-H), 6.13–6.30 (m, 2 H, 1,1′-H), 6.56 (s, 2 H, 4,4′-H), 7.19–7.54 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 51.8 (C-2,2′), 109.2 (C-1,1′), 117.8 (C-3,3′), 126.0 (Ph_{tert}), 127.0 (Ph_{tert}), 128.7 (Ph_{tert}), 132.1 (Ph_{quat}), 140.8 (C-4,4′) ppm. IR (ATR): $\tilde{\nu}$ = 2960, 1632, 1493, 1091, 1042 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 260 (4.34) nm. MS (ESI): *m/z* (%) = 327.1 (75) [M + Na]$^+$, 631.2 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{20}H_{16}O_3Na$ [M + Na]$^+$ 327.0992; found 327.0987.

***N,O*-Bisacetal 26c:** Synthesized by using General Procedure F from diol **25c** (260 mg, 1.02 mmol, 1.0 equiv.) and IBX (627 mg, 2.24 mmol, 2.2 equiv.). Purification: Column chromatography (SiO_2; pentane/EtOAc, 6:1→4:1), yield 108 mg (430 µmol, 42%); colorless oil; R_f = 0.38 (hexane/EtOAc, 2:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 9 H, Me_{Boc}), 3.44 (d, *J* = 6.7 Hz, 2 H, 2,2′-H), 4.89 (dd, *J* = 2.5, 2.5 Hz, 2 H, 3,3′-H), 6.08 (m_c, 2 H, 1,1′-H), 6.23 (br s, 2 H, 4,4′-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.3 (Me_{Boc}), 51.3, 51.4 (C-2,2′), 81.2 ($C_{q,Boc}$), 92.3 (C-1,1′), 102.8 (C-3,3′), 144.4, 144.6 (C-4,4′), 153.1 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 1711, 1619, 1380, 1339, 1133, 1017 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 281 (2.28) nm. MS (ESI): *m/z* (%) = 274.1 (22) [M + Na]$^+$, 525.3 (100) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{13}H_{17}NO_4Na$ [M + Na]$^+$ 274.1050; found 274.1054.

***N,O*-Bisacetal 26d:** Synthesized by using General Procedure F from diol **25d** (19 mg, 47 µmol, 1.0 equiv.) and IBX (29 mg, 103 µmol, 2.2 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 10 mg (25 µmol, 53%); pale-yellow solid; R_f = 0.31 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.56 (s, 9 H, Me_{Boc}), 3.91 (m_c, 2 H, 2,2′-H), 6.12–6.35 (m, 2 H, 1,1′-H), 6.52 (br s, 2 H, 4,4′-H), 7.11–7.36 (m, 10 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.3 (Me_{Boc}), 50.9, 51.1 (C-2,2′), 81.5 ($C_{q,Boc}$), 93.3 (C-1,1′), 117.7 (C-3,3′), 126.2, 126.2, 126.7, 128.5, 128.5 (CH_{Ph}), 132.1, 132.1 (C_{Ph}), 140.9, 141.1 (C-4,4′), 152.9 (CO_{Boc}) ppm. IR (ATR): $\tilde{\nu}$ = 1712, 1636, 1378, 1366, 1098 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 252 (3.87) nm. MS (ESI): *m/z* (%) = 426.2 (100) [M + Na]$^+$, 829.4 (77) [2M + Na]$^+$. HRMS (ESI): calcd for $C_{25}H_{25}NO_4Na$ [M + Na]$^+$ 426.1676; found 426.1669.

Weinreb Amide 28: Synthesized by using General Procedure A from diester **27**[14] (500 mg, 2.94 mmol, 1.0 equiv.), *N,O*-dimethylhydroxylamine hydrochloride (574 mg, 5.88 mmol, 2.0 equiv.), and isopropylmagnesium chloride (2 M in THF, 4.40 mL, 8.82 mmol, 3.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 4:1), yield 370 mg (2.00 mol, 68%); pale-yellow oil; R_f = 0.52 (hexane/EtOAc, 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.53–1.63 (m, 1 H, 5-H), 3.00–3.08 (m, 1 H, 3-H*), 3.20 (s, 3 H, NMe), 3.45–3.53 (m, 1 H, 4-H*), 3.70 (s, 3 H, OMe), 5.85–5.94 (m, 1 H, 2-H), 6.14–6.20 (m, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.4 (C-5), 32.7 (NMe), 34.1 (C-4*), 38.7 (C-3*), 61.8 (OMe), 123.5 (C-2), 127.6 (C-1), 173.8 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 1639, 1418, 1385, 1163, 1093 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 245 (3.67), 208 (3.95) nm. MS (ESI): *m/z* (%) = 186.1 (41) [M + H]$^+$, 208.0 (100) [M + Na]$^+$. HRMS (ESI): calcd for $C_8H_{12}NO_2S$ [M + H]$^+$ 186.0583; found 186.0583.

Thiophene 30a: Synthesized by using General Procedure B from Weinreb amide **28** (160 mg, 864 µmol, 1.0 equiv.) and methylmagnesium chloride (3 M in THF, 0.58 mL, 1.73 mmol, 2.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 7:1), yield 55 mg (392 µmol, 45%); pale-yellow oil; R_f = 0.51 (hexane/EtOAc, 5:1). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20 (s, 3 H, Me), 3.89 (s, 2 H, 5-H), 6.84–7.02 (m, 2 H, 2,4-H), 7.18–7.29 (m, 1 H, 1-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.9 (Me), 44.4 (C-5), 125.1 (C-4*), 126.8 (C-1*), 127.0 (C-2*), 135.2 (C-3), 204.7 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 1710, 1355, 1219, 1160 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1}cm^{-1})] = 236 (3.85), 284 (2.84) nm. MS (ESI): *m/z* (%) = 141.0 (24) [M + H]$^+$, 163.0 (82) [M + Na]$^+$, 303.1 (100) [2M + Na]$^+$. HRMS (ESI): calcd for C_7H_9OS [M + H]$^+$ 141.0369; found 141.0370.

Thiophene 30b: Synthesized by using General Procedure B from Weinreb amide **28** (150 mg, 810 μmol, 1.0 equiv.) and phenylmagnesium chloride (2 M in THF, 0.81 mL, 1.62 mmol, 2.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 4:1), yield 146 mg (722 μmol, 89%); yellow solid; R_f = 0.38 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.49 (s, 2 H, 5-H), 6.80–7.04 (m, 2 H, 2,4-H*), 7.20–7.28 (m, 1 H, 1-H*), 7.42–7.67 (m, 3 H, Ph), 7.98–8.13 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.4 (C-5), 125.0 (C-4*), 126.8 (C-1*), 126.9 (C-2*), 128.5 (Ph_{tert}), 128.7 (Ph_{tert}), 133.3 (Ph_{tert}), 135.5 (Ph_{quat}*), 136.1 (C-3*), 195.9 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 1679, 1447, 1211, 1179 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 197 (4.43), 240 (4.28) nm. MS (EI^+, 70 eV): *m/z* (%) = 202.0 (21) $[M]^+$. HRMS (EI^+): calcd for $C_{12}H_{10}OS$ $[M]^+$ 202.0452; found 202.0453.

Ester 31: To a solution of ester **27**[14] (100 mg, 588 μmol, 1.0 equiv.) in EtOAc (6 mL) and MeOH (6 mL) was added a catalytic amount of palladium on activated charcoal and the mixture was stirred for 16 h at room temperature under a hydrogen atmosphere. After filtration through Celite (EtOAc), the solvents were removed and the product (98 mg, 569 μmol, 97%) was obtained as a pale-yellow solid. R_f = 0.36 (hexane/EtOAc, 10:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.24 (t, *J* = 7.1 Hz, 3 H, Me), 1.64–1.70 (m, 1 H, 5-H*), 2.06–2.23 (m, 1 H, 3-H*), 2.23–2.41 (m, 2 H, 2-H*), 2.44–2.57 (m, 1 H, 4-H*), 2.77–2.96 (m, 2 H, 1-H*), 4.11 (q, *J* = 7.1 Hz, 2 H, CH_2Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.2 (Me), 24.4 (C-5*), 28.6 (C-1*), 31.0 (C-2*), 31.1 (C-3*), 31.9 (C-4*), 60.6 (*C*H_2Me), 172.0 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 2979, 1713, 1401, 1262, 1159, 1043 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 209 (3.75) cm^{-1}. MS (ESI): *m/z* (%) = 173.1 (48) $[M + H]^+$, 195.0 (100) $[M + Na]^+$. HRMS (ESI): calcd for $C_8H_{12}O_2SNa$ $[M + Na]^+$ 195.0450; found 195.0453.

Weinreb Amide 31WA: Synthesized according to General Procedure A from ester **31** (1.00 g, 5.81 mmol, 1.0 equiv.), *N*,*O*-dimethylhydroxylamine hydrochloride (1.13 g, 11.6 mmol, 2.0 equiv.), and isopropylmagnesium chloride (2 M in THF, 8.71 mL, 17.4 mmol, 3.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 4:1), yield 720 mg (3.84 mol, 66%); white solid; R_f = 0.48 (hexane/EtOAc, 1:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.13–2.37 (m, 4 H, 2,3,5-H), 2.52–2.64 (m, 1 H, 1-H_a), 2.77–2.84 (m, 1 H, 4-H), 2.88–2.99 (m, 1 H, 1-H_b), 3.17 (s, 3 H, NMe), 3.71 (s, 3 H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.9 (C-5), 29.1 (C-1), 30.6 (C-3), 30.9 (C-2), 32.0 (C-4), 32.4 (NMe), 61.7 (OMe), 171.7 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 1638, 1421, 1389, 1168, 1103, 1091 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 208 (4.02) nm. MS (ESI): *m/z* (%) = 188.1 (94) $[M + H]^+$, 210.1 (100) $[M + Na]^+$. HRMS (ESI): calcd for $C_8H_{14}NO_2S$ $[M + H]^+$ 188.0740; found 188.0740.

Ketone 32a: Synthesized according to General Procedure B from Weinreb amide **31**-WA (350 mg, 1.87 mmol, 1.0 equiv.), and methylmagnesium chloride (3 M in THF, 1.25 mL, 3.74 mmol, 2.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 5:1), yield 240 mg (1.69 mmol, 90%); pale-yellow oil; R_f = 0.30 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.99–2.42 (m, 7 H, 2,3,5-H,Me), 2.48–2.63 (m, 1 H, 1-H_a), 2.76–2.83 (m, 1 H, 4-H), 2.86–2.98 (m, 1 H, 1-H_b) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 28.8 (C-1), 30.9 (Me), 31.0 (C-2), 32.9 (C-5), 33.5 (C-3), 34.9 (C-4), 205.3 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 1686, 1384, 1352, 1182, 1158 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 227 (3.58) nm. MS (ESI): *m/z* (%) = 143.1 (24) $[M + H]^+$, 165.0 (100) $[M + Na]^+$. HRMS (ESI): calcd for $C_7H_{11}OS$ $[M + H]^+$ 143.0525; found 143.0524.

Ketone 32b: Synthesized according to General Procedure B from Weinreb amide **31**-WA (330 mg, 1.76 mmol, 1.0 equiv.) and phenylmagnesium chloride (2 M in THF, 1.76 mL, 3.52 mmol, 2.0 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 7:1), yield 330 mg (1.62 mmol, 92%); white solid; R_f = 0.55 (hexane/EtOAc, 5:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.13–2.44 (m, 2 H, 2-H), 2.51–2.80 (m, 3 H, 3,4,5-H), 2.91–3.09 (m, 2 H, 1-H), 7.39–7.61 (m, 3 H, Ph), 7.82–8.01 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 29.2 (C-1), 29.6 (C-5), 31.1 (C-2), 34.1 (C-3), 36.3 (C-4), 128.0 (Ph_{tert}), 128.5 (Ph_{tert}), 132.9 (Ph_{tert}), 137.5 (Ph_{quat}), 197.3 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 1643, 1229, 1216, 1042, 1010 cm^{-1}. UV (CH_3CN): λ_{max} [lg(ε/M^{-1} cm^{-1})] = 200 (4.47), 242 (4.16), 275 (3.69) nm. MS (EI^+, 70 eV): *m/z* (%) = 204.1 (29) $[M]^+$. HRMS (EI^+): calcd for $C_{12}H_{12}OS$ $[M]^+$ 204.0609; found 204.0616.

Alcohol 34: Synthesized according to General Procedure D from ester **31** (506 mg, 2.94 mmol, 1.0 equiv.) and $LiAlH_4$ (145 mg, 3.82 mmol, 1.3 equiv.). Purification: flash column chromatography (SiO_2; CH_2Cl_2/MeOH, 10:1), yield 335 mg (2.57 mmol, 88%); pale-yellow oil; R_f = 0.53 (CH_2Cl_2/MeOH, 10:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.08–1.19 (m, 1 H, 5-H), 1.57–1.68 (m, 1 H, 3-H), 1.89 (br s, 1 H, OH), 1.94–2.10 (m, 1 H, 2-H_a), 2.16–2.27 (m, 2 H, 2-H_b,4-H), 2.43–2.58 (m, 1 H, 1-H), 2.79–2.92 (m, 1 H, 1-H), 3.37–3.53 (m, 2 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.0 (C-5), 26.3, 26.4 (C-3,4), 29.7 (C-1), 31.0 (C-2), 64.3 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 1438, 1407, 1239, 1102, 1056, 1012 cm^{-1}. UV (CH_3CN): λ_{max} no absorbance maximum between 190 and 350 nm. MS (ESI): *m/z* (%) = 131.1 (52) $[M + H]^+$, 153.1 (46) $[M + Na]^+$. HRMS (ESI): calcd for $C_6H_{11}OS$ $[M + H]^+$ 131.0525; found 131.0524.

***S*,*O*-Acetal 36:** Synthesized according to General Procedure F from alcohol **34** (307 mg, 2.36 mmol, 1.0 equiv.) and IBX (700 mg, 2.83 mmol, 1.2 equiv.). Purification: flash column chromatography (SiO_2; pentane/EtOAc, 15:1→10:1), yield 4 mg (31 μmol, 1%; product is very volatile); pale-yellow oil; R_f = 0.62 (hexane/EtOAc, 10:1). ^1H NMR (300 MHz, $CDCl_3$): δ = 2.00–2.15 (m, 1 H, 2-H_a), 2.20–2.33 (m, 1 H, 2-H_b), 2.72–2.81 (m, 1 H, 1-H_a), 2.93–3.06 (m, 1 H, 1-H_b), 3.88–4.01 (m, 1 H, 3-H), 4.64–4.79 (m, 1 H, 5-H), 6.21 (d, *J* = 7.8 Hz, 1 H, 4-H), 6.32–6.37 (m, 1 H, 6-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.7 (C-1), 37.8 (C-2), 51.2 (C-3), 94.6 (C-4), 102.9 (C-5), 146.1 (C-6) ppm. IR (ATR): $\tilde{\nu}$ = 2923, 2359, 1632, 1466, 1021 cm^{-1}. UV (CH_3CN): λ_{max} no absorbance maximum between 190 and 350 nm. MS (ESI): *m/z* (%) = 129.0 (4) $[M + H]^+$, 152.1 (100) $[M + Na]^+$. HRMS (ESI): calcd for C_6H_9OS $[M + H]^+$ 129.0369; found 129.0363.

X-ray Crystallography: For the X-ray crystal structures of **20b**, **21c**, and **26a**, a single crystal was mounted with inert oil on a MiTeGen-Loop. The data was collected from the shock-cooled crystals at 100 K. The data for **21c** was collected with a Bruker TXS-Mo rotating anode source with mirror optics and Mo-K_α radiation, λ = 0.71073 Å. The data for **20b** and **26a** was collected with an INCOATEC Ag microsource with mirror optics and AgK_α radiation, λ = 0.56086 Å. Data reduction was done with SAINT,[16a] and an empirical absorption correction with SADABS[16b] was applied. The structures were solved by direct methods (SHELXS-97)[16c] and refined by full-matrix least-squares methods against F^2 (SHELXL-97 and ShelXle).[16c,16d] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in the Supporting Information.

CCDC-925484 (for **26a**), -925485 (for **20b**) and -925486 (for **21c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data for 20b: M_r = 491.56; 0.20×0.15×0.15 mm^3; triclinic; $P\bar{1}$; a = 9.071(2) Å, b = 10.908(2) Å, c = 14.325(3) Å, α = 69.14(2)°, β = 87.03(3)°, γ = 77.38(3)°; V = 1292.0(5) Å^3; Z = 2; ρ_{calc} = 1.264 Mg/m^3; T = 100(2) K; μ(AgK_α) = 0.055 mm^{-1}; $2\theta_{max}$ = 23.269°; 35353 reflections measured, 7554 independent (R_{int} = 0.0357), $R1$ = 0.0409 [$I>2\sigma(I)$], $wR2$ = 0.1107 (all data), res. density peaks: 0.382 and –0.233 e Å^{-3}.

Crystal Data for 21c: M_r = 431.51; 0.15×0.1×0.1 mm^3; triclinic; $P\bar{1}$; a = 8.994(2) Å, b = 9.359(2) Å, c = 14.816(3) Å, α = 80.65(3)°, β = 86.50(3)°, γ = 76.62(2)°; V = 1196.8(4) Å^3; Z = 2; ρ_{calc} = 1.197 Mg/m^3; T = 100(2) K; μ(Mo-K_α) = 0.080 mm^{-1}; $2\theta_{max}$ = 28.312°; 27001 reflections measured, 5926 independent (R_{int} = 0.0345), $R1$ = 0.0392 [$I>2\sigma(I)$], $wR2$ = 0.1023 (all data), res. density peaks: 0.338 and –0.241 e Å^{-3}.

Crystal Data for 26a: M_r = 180.20; 0.20×0.10×0.04 mm^3; orthorhombic; *Fdd*2; a = 10.495(2) Å, b = 24.590(3) Å, c = 6.828(2) Å; V = 1762.1(7) Å^3; Z = 8; ρ_{calc} = 1.358 Mg/m^3; T = 100(2) K; μ(AgK_α) = 0.062 mm^{-1}; $2\theta_{max}$ = 20.493°; 4978 reflections measured, 897 independent (R_{int} = 0.0325), $R1$ = 0.0316 [$I>2\sigma(I)$], $wR2$ = 0.0799 (all data), res. density peaks: 0.156 and –0.143 e Å^{-3}.

Supporting Information (see footnote on the first page of this article): NMR spectra for all new compounds and crystallographic data.

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